MOTOR FUELS

Their Production and Technology

BY

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PREFACE

The subject matter of "Motor Fuels," and the manner in which I have presented it are consequences of several factors. First, I am firmly of the opinion that an accurate knowledge of the fundamental principles of physics, thermodynamics, and chemistry is the all important essential in engineering work. The tendency of the human mind is to travel in ruts, and to follow the line of least resistance. In plant work this frequently results in using no end of ingenuity to perfect, in a mechanical way, an apparatus that may be inherently incorrect, or that at least can never be as efficient as that of another type. There is just one remedy for this. A project or situation should always be subjected to critical analysis on the basis of scientific facts and laws. The result of this investigation will show the feasibility of the project or the true facts of the situation, and will indicate whether or not a change is advisable. With principles and facts clearly in mind it is a relatively easy matter to give these expression in the form of an apparatus or plant. As a consequence of my philosophy, I have presented and have stressed the importance of the fundamental conceptions underlying the operations used in the production of motor fuels.

Second, a work on motor fuels will be of interest to several classes of readers. The non-technical reader will hardly be concerned with the principles of distillation, fluid-flow, or the thermal decomposition of hydrocarbons, but he may be interested in the motor-fuel situation, the general processes used in petroleum refining, the quality of motor-fuels, the future possibilities of alcohol, and so on. I trust that the refinery engineer will find the presentation of the fundamental principles of distillation, fluid-flow, heat-transfer, thermal reactions of hydrocarbons, and refining, of some help, but I can scarcely hope that he will be interested by a brief discussion of general procedures, or by a somewhat more detailed description of apparatus with which he is quite familiar. On the other hand the student who knows little or nothing of refinery technology will find the general and descriptive matter essential to gaining a picture of the industry. I have therefore been confronted with the problem of either limiting the scope of the book to technology, or of making its contents miscellaneous in some measure. I have decided to widen the scope, at the risk of being accused by many readers of including elementary or extraneous material.

Third, as a reader of books I have been led to at least one conclusion with regard to writing books. This is that issues should be faced squarely. Within the limits of my ability and time I have tried to do this, realizing full well the dangers of definiteness in many instances

where knowledge is fragmentary. I trust that in those cases where there is reasonable doubt as to conclusions drawn I have indicated this. In fairness to myself I feel constrained to say that in several instances I have not spoken as freely as I should like because of patent matters.

Fourth, I have intended that "Motor Fuels" should be useful as a reference book, not only on account of the presentation of scientific fundamentals, but because of the review of research work in several fields in which the sum total of present knowledge is still far from satisfactory. An example is the chapter on the thermal reactions of hydrocarbons.

Research is study and investigation designed to extend the boundaries of knowledge. At intervals it is either desirable or necessary to take inventory in order that a balance may be struck in the ledger of knowledge, and a comparison made of what we know and what we should like to know.

To increase the value of "Motor Fuels" as a reference work I have included numerous tables and figures recording important statistical matter or useful data. I have avoided such information as is readily available in standard engineering handbooks and physical and chemical tables or handbooks.

Fifth, I have limited the scope of "Motor Fuels" largely to the production of fuels. While some information has been included on the subject of utilization, this has been only such as applies very directly to the technology of production. Present knowledge of the utilization of fuels is fragmentary, and it will be several years before a comprehensive treatise, other than a review, can be written on this subject.

Sixth, I have purposely omitted discussions of several subjects and tabulations of certain information, or have modified the manner of my own presentation, on account of material contained in works recently published or soon to be published. To be specific, I have omitted a chapter on Storage, Handling, and Transportation because of the information on this subject in Dr. Day's "Handbook of the Petroleum Industry," although I have briefly discussed this subject in Chapter XI.

I have omitted a comprehensive tabulation of the properties of the hydrocarbons. Dr. Day's Handbook contains a lengthy tabulation giving formulas, specific gravities, indices of refraction, boiling points and occurrences of paraffin, olefin, diolefin, acetylene aromatic, naphthene, and terpene hydrocarbons. The tabulation that I had in mind was more comprehensive than that given by Dr. Day in that I intended to include values of more specific physical properties. Although I have many of these data in my personal files, the tremendous amount of work involved in completing and arranging the tables for publication has deterred me.

I had intended to devote another chapter to a formulation of research problems the solution of which would do most to advance

the industry. Both because this subject has recently received much attention at technical society meetings, and because "Motor Fuels," when I arrived at the point of writing this chapter, was already a far larger book than I had intended, I have omitted this chapter.

The portion of Chapter V devoted to heat-transfer phenomena in my opinion leaves much to be desired. I have presented it mainly as a review, and much too non-critically. The available information on this general subject cannot be taken on faith, as much of it is unreliable, not through intention, but because of the experimental methods used, or of oversight of one or more factors. Had I not known that the Chemical Catalog Company was soon to publish a work on Evaporators by Professor W. L. Badger of the Chemical Engineering Department of the University of Michigan, in which book the entire subject of heat-transfer would be critically reviewed, I should have felt constrained to handle this subject in a more elaborate and thoroughgoing manner. To be perfectly frank, I am very much pleased that I can shift the responsibility to my colleague, Professor Badger, and content myself with a brief review, and with the suggestion to the reader who wishes to pursue this subject, that he consult Professor Badger's work.

In writing "Motor Fuels" I have made free use of numerous reference works covering the fields of physics, theoretical chemistry, organic chemistry, and petroleum technology. Among these I wish to mention in particular, Washburn's "Principles of Physical Chemistry," Noyes and Sherrill's "Chemical Principles," and Engler-Höfer's "Das Erdöl."

I am also deeply indebted to many professional men and corporations for their coöperation. While I trust that I have not failed fully to acknowledge this in the context, I wish here to express my appreciation of the valuable assistance of Dr. E. R. Lederer, Dr. C. M. Alexander, Dr. C. J. Greenstreet, Dr. W. F. Rittman, Dr. Roy Cross, and Mr. R. C. Sawyer, and of officials or representatives of The Steere Engineering Company, The U. S. Bureau of Mines, The M. W. Kellogg Company, The Texas Company, The Hope Engineering and Supply Company, The Griscom-Russell Company, The Petroleum Iron Works, The Southwestern Condenser Company, and The S-S-E Company.

I wish to acknowledge my indebtedness to Professor A. H. White, Professor W. L. Badger, Professor E. M. Baker, and to Mr. J. C. Geniesse, of the Chemical Engineering Department of the University of Michigan, for their valuable suggestions and advice.

In particular I am indebted to Professor Baker, who worked with me in the preparation of the larger part of the manuscript of Chapter IV on fractional distillation.

In conclusion, may I say that I shall appreciate suggestions that will enable me to make "Motor Fuels" a more useful book.

E. H. Leslie.

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MOTOR FUELS

Chapter I.

The Motor Fuel Problem.

The problem of ensuring an adequate future supply of motor fuel is one that should engage the serious thought of all who guide the forces of production and consumption of this important commodity. We have been frequently reminded by scientific men that a time is approaching when the production of petroleum in this country must decline. As has been said by Dr. George Otis Smith, "The motto inscribed on our silver coins should hardly be made a national policy in providing a future oil supply." But in every period of abundant and increasing supply of crude oil the public is lulled into a sense of security by the carelessly conceived writings of newspaper and trade-paper journalists, who scout the opinions of their more far-sighted and better informed scientific friends. In the meantime the large corporations of foreign lands, with government aid when necessary, proceed quietly to obtain concessions and valuable exclusive rights whenever and wherever possible.

The problem with which we are concerned is the source of our future motor fuel supply. Not that for next year, nor for the next five years, but for the years that are probably not more than ten years away. How much fuel will be needed, and how shall it be obtained at reasonable cost? Part of this book will be devoted to offering an answer to these questions.

To start with, one must distinguish between the long range view-point of the scientist or executive, and the short-range view-point of the newspaper journalist who sees only the temporary aspects of the situation. The petroleum industry cannot escape the forces of the business cycle. The ups and downs of prices and production are the result. These changes would occur even if there were an inexhaustible supply of oil below ground. The real problem exists because of the limited extent of a natural resource—petroleum. It is being used rapidly. What are we going to do about it? This is the broad problem of which the motor fuel problem is a part.

Doubtless, extensive changes will be made in the design of automotive equipment, along with far-reaching readjustments in the industries that supply the fuels. It is not surprising that the Society of Automotive Engineers and the National Automobile Chamber of Com-

merce took the lead in efforts to coördinate the developmental activit of the producers and consumers of motor fuels. The life of the au motive industries depends on the availability of cheap suitable fuels.

On June 4, 1919, a joint meeting of representatives of the afo: mentioned organizations, and representatives of the then newly-form American Petroleum Institute, was held. A committee consisting ten members, five selected by the American Petroleum Institute a five jointly by the Society of Automotive Engineers and the Natio Automobile Chamber of Commerce, was appointed to make constructi plans for the future. At a meeting of this committee held August : 1919, a resolution was adopted urging flexible motor fuel specificatio and recommending extensive research work in the fields of producti and utilization. The research program of the Society of Automoti Engineers is to start at the U. S. Bureau of Standards in the shape an investigation of the effect of volatility of gasoline on fuel consur tion. This work will also receive financial support from the Natio Automobile Chamber of Commerce. So the problem has receiv recognition, and the first steps are being taken for its solution.

The Growth of the Automotive Industries.

The rapid growth of the automotive industries is shown in Tab I, II, and III that follow. These data, except as otherwise noted, a taken from "Facts and Figures," the annual statistical publication the National Automobile Chamber of Commerce.

According to the statistics given on page 52 of "Facts and Figure for 1922, the world registration of motor vehicles at the beginni of the year 1922 was 12,528,272. 83 per cent of these were the United States. When one considers that only twenty-five yea ago there were only four automobiles in the country, one in a circ

TABLE I

GENERAL STATISTICS OF THE AUTOMOTIVE INDUSTRY

Year	1899	1904	1909	1914	1919
Capital Invested	$5,769,000	$23,084,000	$173,837,000	$407,730,000	$1,802,302,0
Number of Motor Vehicles Produced	3,700	21,975	127,731	569,045	1,974,016
Value of Motor Vehicles Produced ..	$4,748,000	$30,034,000	$249,202,000	$632,831,000	$2,506,834,0
Persons Engaged in Manufacture	....	13,338	85,359	145,951	651,450
Wages and Salaries ...	$1,616,000	$8,416,000	$58,173,000	$139,453,000	$813,731,0

TABLE II

PRODUCTION OF PASSENGER CARS AND MOTOR TRUCKS

Year	Passenger Cars	Motor Trucks	Combined Passenger Car and Motor Trucks
1899	3,700	....	3,700
1904	21,281	411	21,692
1909	127,731	3,255	130,986
1910	181,000	6,000	187,000
1911	199,319	10,655	209,974
1912	356,000	22,000	378,000
1913	461,500	23,500	485,000
1914	543,679	25,375	569,054
1915	818,618	74,000	892,618
1916	1,493,617	90,000	1,583,617
1917	1,740,792	128,157	1,868,949
1918	926,388	227,250	1,153,638
1919	1,657,652	316,364	1,974,016
1920	1,883,158	322,039	2,205,197
1921	1,514,000	154,550	1,668,550

TABLE III

REGISTRATION OF MOTOR VEHICLES IN THE UNITED STATES

December 31, of the Year	Number of Vehicles (estimated)
1899	10,000
1904	85,000
1909	400,000
1910	600,000
1911	677,000
1912	1,010,483
1913	1,253,875
1914	1,711,339
1915	2,445,664
1916	3,512,996
1917	4,983,340
1918	6,146,617
1919	7,558,848
1920	9,211,295
1921	10,448,632

another used for exhibitions, and two that were looked upon as mechanical freaks, the existence of the present total of ten and one-half million is almost unbelievable. The increase in the rate of production has been rapid. In 1914 there were four and one-half times as many cars and trucks manufactured as in 1909, and in 1919 three times as many as in 1914. Obviously this rate of growth cannot continue. In fact we must now regard the motor vehicle industries as being in a transitional stage of their development. Heretofore a very large part of the cars passed into the hands of buyers who had never before

owned a car. In a few years the larger part of the business will b
replacement sales, and the smaller part, which will be roughly propo
tional to the growth in population of the country, will be new busines

Passenger cars and trucks use between seventy-five and eighty pe
cent of the gasoline consumed in this country. The other twent
per cent is used in stationary engines, tractors, airplanes, power boat
and for miscellaneous purposes as a solvent. We may expect to se
a marked increase in the number of pleasure cars, trucks, tractors, an
airplanes, and hence a demand for more fuel.

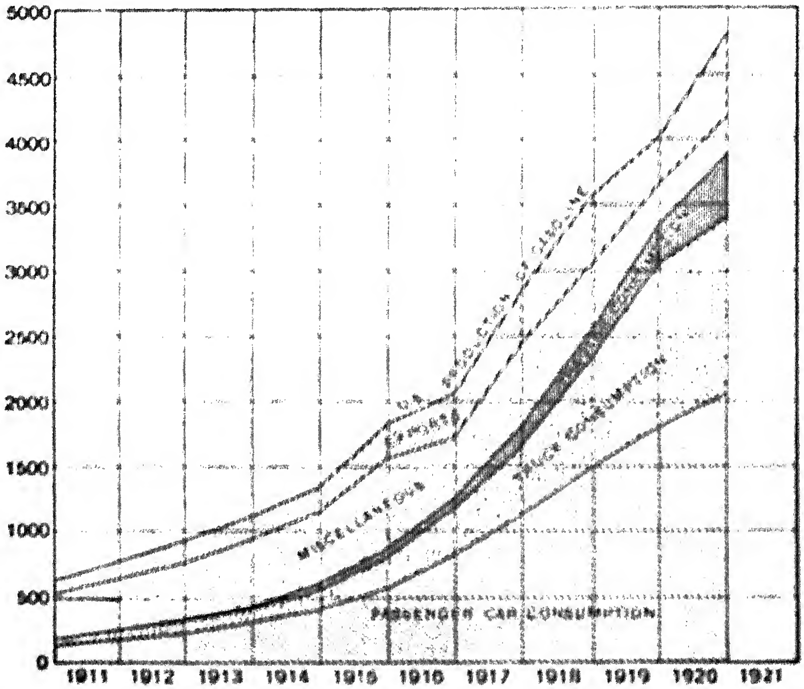


FIG. 1.—Analysis of the Growth in the Demand for Gasoline in the Unite
States, 1910-1920

To summarize, it is evident that the future will require the produc
tion of a far larger quantity of motor fuel than is at present availabl
If it is assumed that the future total number of cars and trucks b
stabilized at the conservative figure of 13,000,000, that these vehicle
consume 75 per cent of the total fuel, and that the exportation o
gasoline be the same as at present, the total gasoline requirement wi
be slightly less than seven billion gallons. The present total consump
tion and exportation of gasoline is between four and one-half an
five million gallons. Just what would happen if even a small part o
the rest of the world should take a notion to become motorized to a

extent approaching that of the United States is an interesting speculation.

Figure 1 from Dr. Pogue's "Economics of Petroleum," shows the relative importance of various factors that have caused the increasing demand for gasoline. The figure is based on the statistical results of an investigation conducted by the War Industries Board in 1918, and on the assumption that each pleasure car consumes 335 gallons of gasoline and each truck 1,000 gallons of gasoline annually. The same data, but calculated to a percentage basis, are shown in Figure 2, also given by Dr. Pogue.

Sources of Petroleum Statistics.

Starting with 1918 the U. S. Bureau of Mines has compiled and issued monthly statistics covering the petroleum refining industry. These include figures for crude oil run, oil re-run, and for gasoline, kerosene, gas- and fuel-oil, lubricating oil, wax, coke, asphalt and miscellaneous products. The data are compiled for several districts designated as (1) East Coast, (2) Pennsylvania-New York Eastern Ohio-West Virginia, (3) Western Ohio-Indiana-Illinois-Kentucky-Tennessee, (4) Oklahoma-Kansas, (5) Texas, (6) Louisiana-Arkansas, (7) Colorado-Wyoming, and (8) California. Yearly summaries and analyses are also given.

The U. S. Geological Survey issues monthly and annually statistical data covering the production of crude oil in the various fields, and pipe-line runs and storage. The annual summaries are published as parts of "Mineral Resources." The current statistics of the Survey are based on the quantity of petroleum *transported* from producing properties. Oil consumed on the leases is not included. This item and the change in producers' stocks are obtained by an annual canvass. The yearly statistics are corrected therefor.

The weekly bulletins of the American Petroleum Institute contain estimates of the daily average crude oil production of the various districts in the several fields. These estimates are based on telegraphic advices from the various companies that maintain scouting organizations. The companies making the reports are under no obligation to do so, but do it as a matter of public service. Differences between the statistics of the U. S. Geological Survey and the American Petroleum Institute are the result of the fact that there may be a difference between oil "produced" and oil "transported." Over a long period, however, the statistics of these organizations will agree closely.

The U. S. Bureau of Foreign and Domestic Commerce issues monthly summaries of the imports and exports of petroleum and its products.

The Production of Gasoline.

In Table IV statistics are presented covering the production of gasoline in the United States, the imports of gasoline, the domestic

consumption of gasoline, the exports of gasoline, and the percentage of gasoline obtained from crude oil. Imports were of little consequence prior to 1915. The consumption is calculated by adding together production and imports, subtracting exports, and in those years for which the statistics are available, correcting the result for the change in stocks during the year.

TABLE IV

GASOLINE STATISTICS

Year	Production of Gasoline in United States (Bbls. of 42 gals.)	Imports of Gasoline into United States (Bbls. of 42 gals.)	Exports of Gasoline from United States (Bbls. of 42 gals.)	Consumption of Gasoline in United States and Insular Possessions (Bbls. of 42 gals.)	Per cent of Gasoline Obtained from Crude Oil
1899	6,680,000[a]	....	[illegible]	[illegible]	
1904	6,920,000[a]	.....	[illegible]	[illegible]	
1909	12,900,000[a]	.....	[illegible]	[illegible]	[illegible]
1914	34,915,000[a]	.....	[illegible]	[illegible]	[illegible]
1915	41,600,000[b]	[illegible]	[illegible]	[illegible]	[illegible]
1916	49,020,[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
1917	67,870,150[c]	248,900[c]	[illegible]	[illegible]	[illegible]
1918	85,007,450[d]	307,127[e]	[illegible]	[illegible]	[illegible]
1919	94,234,690[d]	212,861[e]	[illegible]	[illegible]	[illegible]
1920	116,251,110[d]	1,060,812[e]	[illegible]	[illegible]	[illegible]
1921	122,703,555[d]	[illegible]	[illegible]	[illegible]	[illegible]

[a] Data from Senate Document 310, 65th Congress, 1st Session, compiled by Bureau of the Census.

[b] Estimated for Senate Document 310, 65th Congress, 1st Session, by U. S. Geological Survey.

[c] Figures of U. S. Geological Survey.

[d] Figures of U. S. Bureau of Mines.

[e] Figures of the U. S. Bureau of Foreign and Domestic Commerce.

[f] These figures are corrected for changes during the year in refined stocks on hand.

The increase in the production of gasoline is little less than marvelous. In the six year period, 1915-1921, the output nearly trebled. But the registration of motor vehicles increased even more, for on December 31, 1921, there were 4.27 times as many vehicles registered as on December 31, 1915.

The ratio between gasoline production and motor vehicle registration, and between gasoline consumption and vehicle registration, is shown in Table V.

The proportion of the total gasoline that is consumed by motor vehicles lies between 75 and 80 per cent, so that to obtain an approximate idea as to the actual annual gasoline consumption per vehicle it is necessary to multiply the figures given in the second column by 0.75. Undoubtedly, the use of each vehicle is greater today than it

TABLE V

Gasoline Produced and Consumed per Motor Vehicle

Year	Barrels of Gasoline Produced per Motor Vehicle in Operation	Barrels of Gasoline Consumed per Motor Vehicle in Operation
1915	17.0	11.3
1916	13.9	11.5
1917	13.6	11.2
1918	13.8	12.1
1919	12.8	11.9
1920	13.0	11.4
1921	11.7	10.4

was a few years ago. Hence the fact that the barrels of fuel consumed per vehicle per year has been nearly constant since 1916, or has

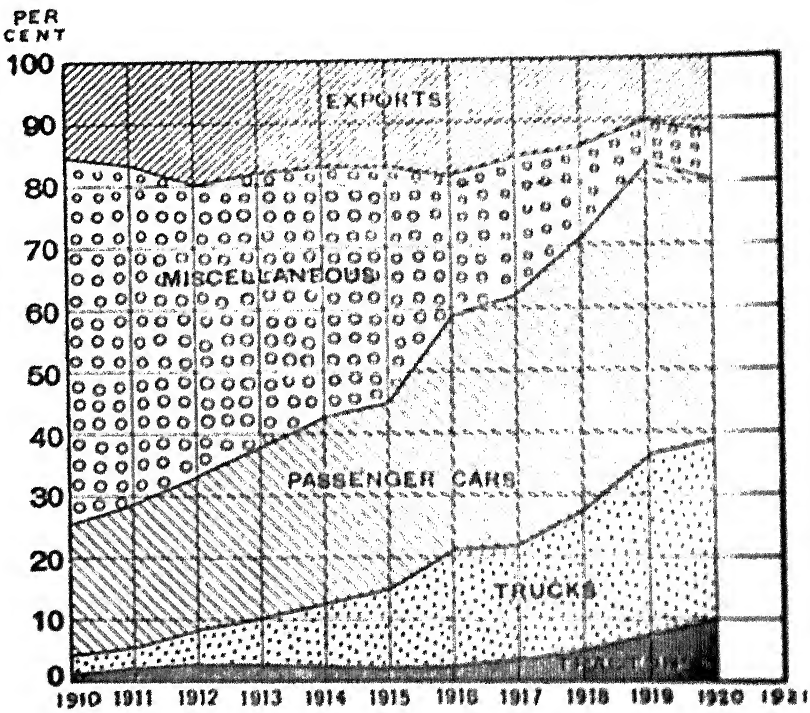


Fig. 2.—Percentage Analysis of the Demand for Gasoline, 1910-1920

decreased, shows that the fuel is more effectively utilized today than it was a few years ago.

It is probably fair to say that a fuel problem has been recognized for about five years. To increase the proportion of gasoline obtained

from crude oil to 20 per cent was fairly easy. In Figure 1[1] the curve DBE shows actual gasoline production, and ABC [illegible] would have been if the gasoline yield had been [illegible] per cent of the crude by volume. The ordinates between the curves AB and DB represent gasoline that could have been [illegible]. The ordinates between line BE and BC represent gasoline [illegible] produced with difficulty, and only because of the great demand for the product. The point B at which the curves [illegible] may be taken as showing the time when the gasoline problem became acute enough to attract general attention.

How has the supply of gasoline been increased [illegible]? Will it be possible to continue the increase in supply [illegible] by the methods already used, or other means which may be developed? The answer to these questions necessitates a study of each of the factors involved.

The present production of gasoline has been made possible by increasing production of crude oil, by marketing a product of wider distillation range, by developing the natural gas gasoline industry, by applying cracking processes to the kerosene, by blending [illegible] distillates with gasoline, by importing petroleum from foreign countries, and by the fact that the crude oils distilled in recent years have contained a larger proportion of gasoline than those produced ten years ago. In addition to these, other means will be used in the future, the most important of which will be the production of alcohol. A shale oil industry may be developed in the near future. Further than this, changes in the automotive industries will have their effect. We may expect important developments in the line of more efficient fuel utilization both because of mechanical changes in the engine and accessory devices, and because it is now more generally recognized that investigation of the chemistry of the combustion process has been sadly neglected. A careful study of combustion may point the way to the satisfactory use of kerosene. Heavy oil engines are a distinct future possibility. Also, the steam car, that curiously neglected member of the automotive family, must surely receive further attention. All of these possible developments in the consuming industry are the equivalents of an increase in the output of motor fuel.

Production of Crude Petroleum in the United States.

The domestic production of crude oil is the basis of our motor fuel supply. Table VI presents the figures of the U. S. Geological Survey for the marketed production of crude oil for each of the last thirteen years.

How long will it be possible to increase domestic petroleum production to meet the growing needs? This question has been in the minds of students of the situation for many years. Several estimates

[1] A graphical showing similar to Figure 1 has been given by Pogue, Dr. J. E. See Automotive Industries, 40 (1919), p. 1319, et seq.

TABLE VI

Marketed Production of Crude Oil in the United States

Year	Barrels of 42 Gallons
1908	178,527,355
1909	183,170,874
1910	209,557,248
1911	220,449,391
1912	222,935,044
1913	248,446,230
1914	265,762,535
1915	281,104,104
1916	300,767,158
1917	335,315,601
1918	355,927,716
1919	377,719,000
1920	443,402,000
1921	469,639,000

of the petroleum reserve of the United States have been made. In March, 1921, the U. S. Geological Survey invited the American Association of Petroleum Geologists to coöperate with the Survey in an effort to estimate the extent of producing, probable, and possible oil territory of the United States. The invitation was promptly accepted. The Committee responsible for the original preparation of the estimates and for the final adjustment and revision of the results consisted of F. W. DeWolf, W. E. Wrather, Rowell H. Johnson, Wallace A. Pratt, Alexander W. McCoy, Carl H. Beal, C. T. Lupton, Alexander Deussen, K. C. Heald, and G. C. Matson, all of the Association, and David White, Chairman, W. T. Thom, Jr., A. E. Fath, K. F. Mather, and R. C. Moore, of the Survey. Mr. Heald also represented the Survey. These men were assisted by other eminent geologists from oil companies and State Surveys, and by many consulting geologists.

The calculations of the reserve in proved fields are believed to be reasonably reliable, and those covering "probable" fields are based on the best information available and should be fairly accurate. The estimates of oil reserves in "possible" territory are "absolutely speculative and hazardous" and "although they represent the best judgment of the geologists, they nevertheless may be, at least in part, wildly erroneous." The quotations above and those that follow are from the report of the Committee. The estimate of the Committee, shown in Table VII, is undoubtedly the most accurate estimate that has been made, and is to be regarded as conservative. Of the nine billion barrels, five billion is oil in sight, and four billion oil that will "probably" and possibly be found. Somewhat over four billion barrels is of the heavy oil type, and will be found mainly in the Pacific Coast, Rocky Mountain, and Gulf States. The reserve of paraffin and mixed base oils of good grade amounts to five billion barrels, of which seven hundred and twenty-five million barrels is of the high-grade type found in the Appalachian regions.

The Committee expres[illegible] the estimated reserves appear to be [illegible] if consumed at the present rate, the [illegible] of this period. The oil pools will [illegible] twenty years, and wells cannot be pumped [illegible] wells will yield oil for more than a quarter [illegible]

TABLE VII

ESTIMATED OIL R[illegible]

	Barrels [illegible]
New York	[illegible]
Pennsylvania	[illegible]
West Virginia	[illegible]
Ohio	[illegible]
Indiana and Michigan	[illegible]
Illinois	[illegible]
Kentucky, Tennessee, Northern Alabama, and North-eastern Mississippi	[illegible]
Missouri, Iowa, South Dakota, Wisconsin, and Minnesota	[illegible]
Kansas	[illegible]
Oklahoma	[illegible]
Northern Louisiana and Arkansas	[illegible]
Texas, except Gulf Coast	[illegible]
Gulf Coast of Texas and Louisiana	[illegible]
Colorado, New Mexico, Arizona	[illegible]
Wyoming	[illegible]
Montana, Nebraska, and South Dakota	[illegible]
Utah, Nevada, Oregon, Washington, Idaho	[illegible]
California	[illegible]
Eastern Gulf Coastal Plain and Atlantic Coast States	[illegible]
Total	[illegible]

wells will not have been drilled in [illegible]. In short, the oil cannot all be discovered, much less taken from the earth in twenty years. The United States is already absolutely dependent on foreign countries to eke out her own production, and if foreign oil can be procured, this dependence is sure to grow greater and greater as our own fields wane.

"All the estimates, except those for one region, noted below, include only oil recoverable from the ground by present methods, but it is practically certain that the percentage of oil to be recovered from American oil-fields will be vastly increased by the application of new and improved methods of recovery. Little has been determined as to the applicability of 'air pressure,' 'water drive,' 'gas-pressure,' 'vacuum-extraction,' and other new methods. At present, any estimates of such possible additional recoveries would probably contain errors enormously greater than those inherent in the estimates made on the basis of the methods now in use.

"In only one region are the geologic conditions so well known, and

the experience with improved methods on a commercial basis so extensive and so long continued, as to justify the formulation of estimates based on results obtained. This is the region in northwestern Pennsylvania and southwestern New York, where the 'water-drive' is now employed to obtain oil from the Bradford sand, which was supposed to be largely exhausted. Under the peculiar conditions there, the use of this method will result in the recovery of a large quantity of oil that cannot be recovered by ordinary methods of production. Allowance for the additional oil thus recovered has therefore been made in the estimates. It has already been found, however, that this method is not applicable to some other districts.

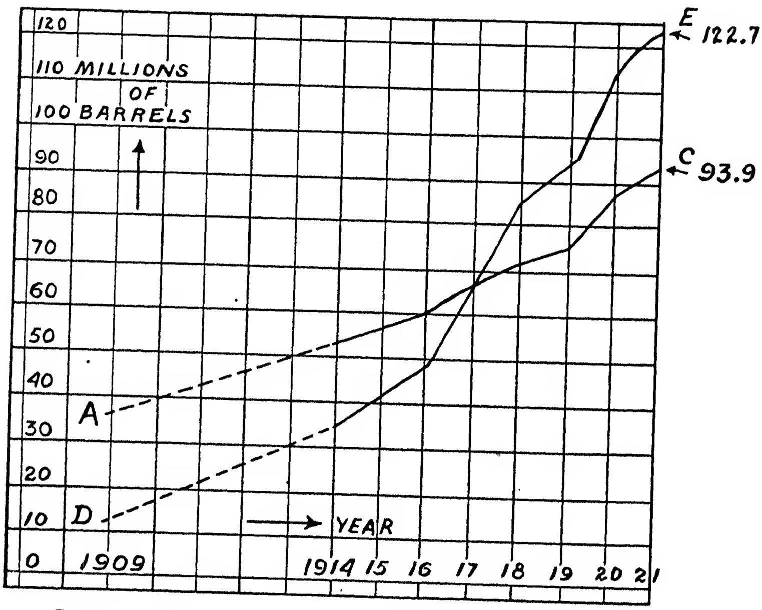


FIG. 3.—Gasoline Production. Curve DBE—Actual. Curve ABC—20% of Crude.

"The joint committee points out the stern obligation of the citizen, the producer, and the Government to give most serious study to the more complete extraction of the oil from the ground, as well as the avoidance of waste, either through direct losses or through misuse of crude-oil or its products."

Importation of Petroleum.

The United States, for many years, has produced between three-fifths and two-thirds of the world's petroleum. But in spite of this tremendous production we have drawn largely on foreign sources of

supply. Importations have increased rapidly in the last three years. In 1921 imports were almost 27 per cent of domestic production, and were fifty-four million barrels in excess of combined exports of petroleum and all its products. Table VIII shows the annual imports and exports of petroleum from 1913 to 1921 inclusive.

TABLE VIII

IMPORTS AND EXPORTS OF CRUDE PETROLEUM

(BARRELS OF 42 GALLONS)

Year	Imports	Exports	Difference
1913	17,809,000	4,620,000	13,189,000
1914	17,247,000	2,970,000	14,277,000
1915	18,140,000	3,765,000	14,375,000
1916	20,570,000	4,100,000	16,470,000
1917	30,162,000	4,098,000	26,064,000
1918	37,736,000	4,900,000	32,836,000
1919	52,747,000	5,924,000	46,823,000
1920	106,175,000	8,045,000	98,130,000
1921	125,307,000	8,940,000	116,367,000

Foreign Petroleum Supplies.

This country is now dependent in large degree upon foreign supplies of crude oil, and year by year is becoming more dependent. Are we to wake up a few years hence to find that through the energy and far-sightedness of foreign corporations and Governments the opportunity to develop valuable producing properties abroad is closed to us, or, at least, that the richest and most easily developed oil lands are no longer available? The writer does not feel himself competent to discuss the international aspects of the petroleum industry, and so will only briefly refer [a] to some of the more important recent publications on the subject.

The foreign countries that have shown the most active interest in oil supplies are Great Britain, The Netherlands, France, Japan, and

[a] Knapp, I. N., "An Optimistic View of the Future Supply of Oil." *J. Eng. Club of Phila.*, 35 (1918), 22-32.

"Report of the Secretary of the Interior on International Policies Affecting the World's Petroleum Industry"—*Congressional Record*, July 29, 1919.

Smith, George Otis, "A World View of the Oil Supply." *Eng. Min. J.*, 110 (1920), 1047-49.

Manning, Van H., "International Aspects of the Petroleum Industry." *Bull. Am. Inst. Min. Met. Eng.*, 1920.

White, David, "The Petroleum Resources of the World." *Ann. Am. Ac. Pol. & Social Service*, May, 1920.

Smith, George Otis, "A Foreign Oil Supply for the United States." *Bull. Am. Inst. Min. Met. Eng.*, 1920.

O'Donnell, Thomas, "World Petroleum Conditions." *Bull. Am. Pet. Inst.*, No. 200, Dec. 21, 1921.

White, David, "Our Future Oil Supply." *Eng. Min. J.*, 111 (1921), 951-55.

(*Footnote continued on following page.*)

The Argentine. Many conflicting statements have been printed referring to the activities of these countries and to the present and future position of the United States. The following quotations from the British press are of interest. The *Financial News* (London) of February 24, 1920, says:

"At the commencement of the war, we believed that the effective British share of the oil resources of the world was about 2 per cent. Careful Admiralty calculations, recently made, have shown that it is now about 56 per cent. This figure includes the Persian and Burmah resources, but takes no account of the vast South American fields commanded by the British Controlled Oil fields. The exact amount of their contribution cannot, at the moment, be estimated with anything like precision. Probably a modest estimate might put it at another 19 per cent. If that be so, our present command of the world's oil resources runs to no less than 75 per cent of their entirety." And we sometimes accuse our British cousins of being slow!

A similar view is given by the British economist, E. Mackay Edgar, in *Sperling's Journal* for September, 1919. He points out our profligate handling of our oil resource, mentions that the Royal Dutch and Shell groups alone control a fourth of the world's oil, and says, "America is running through her stores of domestic oil and is obliged to look abroad for future reserves, and these reserves, constituting a key position in international industry, are very largely in British hands or controlled by British capital. Before very long America will have to come to us for the petroleum she needs.

"We shall have to wait a few years yet before the full advantage of the situation begins to be realized. But that the harvest will eventually be a great one can be no matter of doubt.

"It will be within the limits of the commanding position that the future has in store for us to hold up the entire world to ransom in the distribution and the price of this vital essential."

These views are quite in contrast to those expressed by British politicians who hold that only a very small part of the world's oil is controlled by Great Britain; and that the United States now holds a near-monopoly. As is pointed out by David White, there is much truth in both of these view-points, for the economists refer to the future, and the politicians are talking about the present. One should

Doheny, E. L., "Mexico—The Future of Its Oil Business." *Bull. Am. Pet. Inst., No. 200, Dec. 21, 1921.*

Cadman, Sir John, "Great Britain and Petroleum." *Bull. Am. Pet. Inst., No. 200, Dec. 21, 1921.*

Latane, J. H., "American Foreign Policy." *World's Work*, 41 (1921), 505-511.

Bedford, A. C., "What the Oil Situation Means to Future Business." *Leslie's Weekly*, 132, Jan. 1 (1921), 25-26.

Arnold, Ralph, "The Oil Situation." *Min. Met.*, March, 1921, 20-21.

Manning, Van H., "Uncle Sam's Side of the Bargain." *Nation's Business*, 9, June, 1921, 16-17.

Lewis, J. O., "America's Petroleum Problem." *J. Fr. Inst.*, 191 (1921), 357-379.

clearly distinguish between control of reserve supplies and present control of commercial production.

Until 1920 there was no restriction imposed limiting the activity of foreign oil-corporations in this country. The leasing law of 1920 contained a retaliatory provision to the effect that companies in the control of nationals of another country that excludes our companies from operating in territory in the control of that country may be excluded from operation in the "public lands" of the United States.

In referring to the statements of Sir John Cadman, Lord Curzon, and other British writers who have dilated on the present position of the United States, David White[3] says,

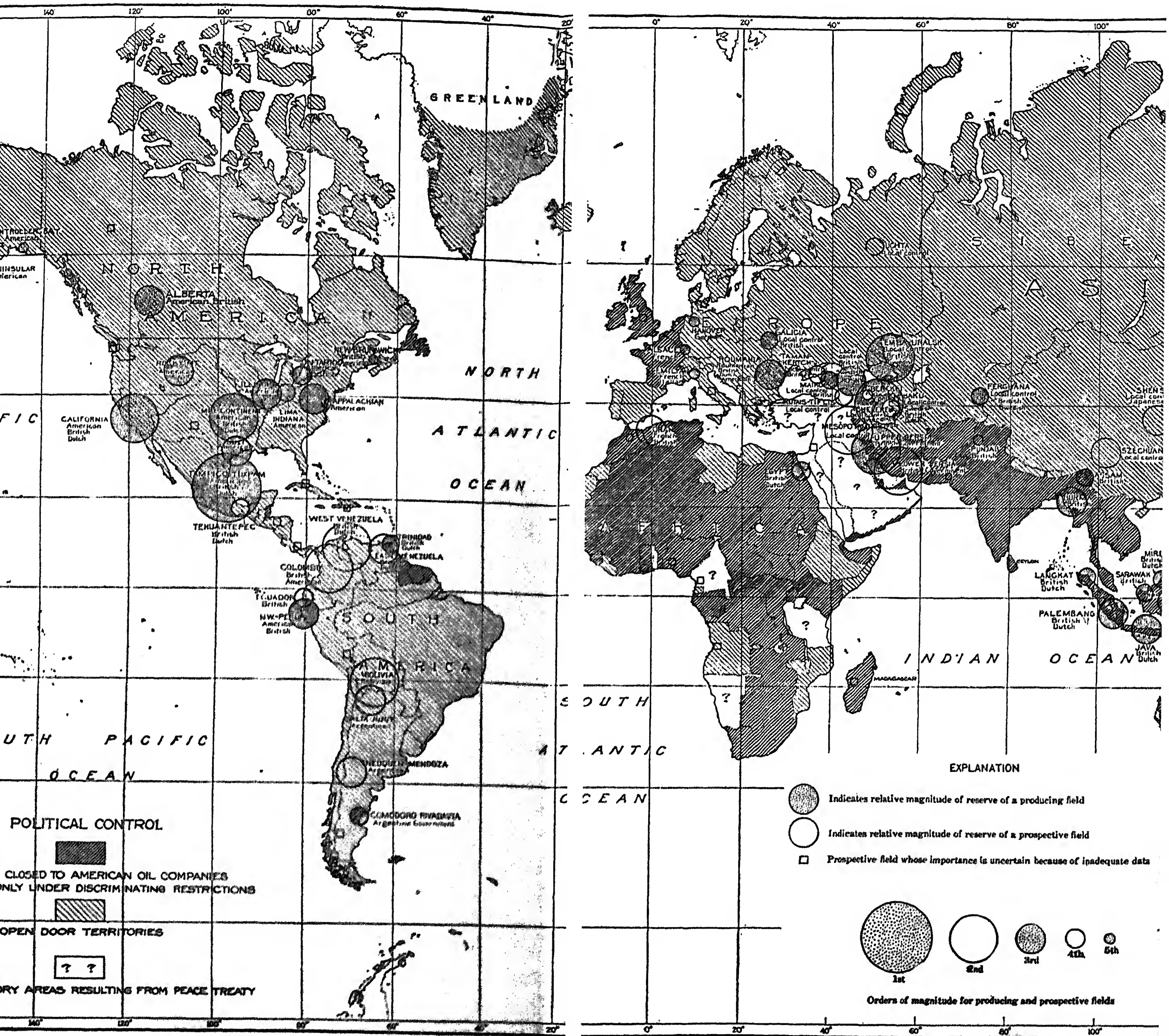
"These seductive statements have soothed the apprehensions of many American hearers, and have served as the foundation for many misleading American editorials. The real issue—the question of oil for America when our fields are exhausted—is, so far as possible, skillfully dodged." And further, "It is common knowledge that our principal allies, now our commercial rivals and competitors, have by secret agreements, by diplomatic camouflage, and by direct action, shown a purpose to close to us the open door of equal opportunity in the mandatory as well as in other countries under their influence, and to hasten the day when we may be dependent on them for oil. Oil is essential to our work, to our daily living, and to our protection. In the day of our disadvantage and dependence can we expect fairer treatment than we are receiving now?" David White's paper is worth the most careful perusal.

Not only is the United States faced with the political and commercial rivalry of several of the great nations of the world, but also by a noticeable tendency on the part of the smaller nations to vest in the State the control of the petroleum resource. This tendency toward nationalization is particularly apparent in the policies of the nations of Central and South America. Just exactly how much of a barrier to development this may be is yet to be seen, but it is at least probable that it will not make petroleum cheaper in the United States.

Since the needs of this country require that oil be imported, it is important to inquire as to the extent of the petroleum resources of the rest of the world. Obviously if it is impossible accurately to estimate domestic resources, any statement of world resources can be little more than a carefully considered guess. Dr. Eugene Stebinger has prepared such an estimate of oil in sight for the United States Geological Survey. His figures are given in Table IX. A map, also prepared by Dr. Stebinger, in 1919, showing relative magnitudes of producing and prospective fields as well as political control is shown in Figure 4.

At present the production of oil in Mexico is the matter of greatest concern to this country, as any change in Mexican conditions will have an immediate effect in this country. Dr. Ralph Arnold[4] believes

[3] *Eng. Min. J.*, 111 (1921), 951.
[4] *Mag. of Wall Street*, April 2, 1921, 782-3.



WORLD MAP OF DEVELOPED AND P TENTIAL PETROLEUM RESERVES

PREPARED BY THE U. S. :OLOGICAL SURVEY

1919

COMPILED BY EU NE STEBINGER

FIG. .

that the latter part of the year 1922 will see the end of the large proven fields of Mexico. A similar opinion is expressed by Dorsey Hager.[8] To discuss the present situation in Mexico in these pages is useless, as

TABLE IX

OIL RESOURCES OF THE WORLD

Country or Region	Relative Value	Millions of Barrels
United States and Alaska	1.00	7,000
Canada	.14	995
Mexico	.65	4,525
Northern South America including Peru	.82	5,740
Southern South America including Bolivia	.51	3,550
Algeria and Egypt	.13	925
Persia and Mesopotamia	.83	5,820
Southeastern Russia, Southwestern Siberia and the Region of the Caucasus	.83	5,840
Roumania, Galicia, and Western Europe	.16	1,135
Northern Russia and Saghalien	.13	925
Japan and Formosa	.18	1,245
China	.20	1,375
India	.14	995
East Indies	.43	3,015
Total	6.15	43,055
Total Eastern Hemisphere	3.03	21,255
" Western "	3.12	21,800
" North of the Equator	5.20	37,400
" South " " "	.95	6,655

the matter may easily be settled before these paragraphs appear in print. A very interesting account of the development of the industry in Mexico is given by Edward L. Doheny.[9] His views of Mexico as a future producer are most optimistic. In his 1920 report to the stockholders of the Mexican Petroleum Company, Mr. Doheny says, "The dire predictions of the ill-informed, even though educated, experts, indicates a predilection to pessimistic forebodings, due to their own successive disappointing experiences."

All in all it appears probable that although current production may temporarily fail as a result of the encroachment of salt water and lack of time to develop new fields, the future will find Mexico a substantial producer as a result of the development of new oil-regions. The work of extending the Mexican fields is in active progress today. Mexican oil production and exports are shown in Table X.

[8] *Nat. Pet. News*, Feb. 16, 1922.
[9] *Bull. No. 200, Am. Pet. Inst.*, Dec. 21, 1921.

TABLE X

[illegible]

Year	[illegible]	[illegible]
1917	[illegible]	[illegible]
1918	[illegible]	[illegible]
1919	[illegible]	[illegible]
1920	[illegible]	[illegible]
1921	[illegible]	[illegible]

The American Petroleum Institute[1] has estimated the world's production of petroleum in 1921 as 730,030,000 barrels. The U. S. Geological Survey reported a world production of 694,854,000 barrels for 1920. The indicated increase for 1921 is 5.2 per cent. Mexico's output increased 19.4 per cent over that of 1920. The United States produced 61.9 per cent of the world's oil, and the United States and Mexico together 87.6 per cent of the total. Table XI gives the world statistics for 1920 and 1921.

TABLE XI

ESTIMATED PETROLEUM PRODUCTION OF THE WORLD

Country	1921 Barrels	1920 Barrels
United States	469,639,000	443,402,000
Mexico	195,064,000	163,540,000
Russia	28,500,000	25,429,000
Dutch East Indies	18,000,000	17,529,210
Persia	14,000,000	12,352,655
Roumania	8,347,000	7,435,344
India	6,864,000	7,500,000
Poland (Galicia)	3,665,000	5,606,116
Peru	3,568,000	2,816,649
Japan and Formosa	2,600,000	2,139,777
Trinidad	2,354,000	2,083,027
Argentina	1,747,000	1,665,980
Egypt	1,181,000	1,042,000
Venezuela	1,078,000	456,926
F...	392,000	388,700
...ny	200,000	212,046
...i	190,000	196,937
[illegible]	35,000	34,180
...a	3,000	3,916
...und	3,000	2,909
...s	1,000,000	1,015,949
...otal	730,030,000	694,895,000

...ral-Gas Gasoline.

...he natural-gas gasoline industry has been an important factor in ...lying motor fuel to meet the increasing need. The industry is of

[1] *Bull. Am. Pet. Inst.*, 3 (1922), No. 10.

so much importance that a separate chapter is devoted to its growth, technology, and prospects. Reference should therefore be made to Chapter XI.

The importance of natural-gas gasoline is not to be measured alone by the volume of this product produced, for the use of natural-gas gasoline in blending practice makes it possible to market, as part of blended gasolines, naphthas that could not be marketed as gasoline.

The natural-gas gasoline industry is only a little over ten years old. Starting about 1910 it grew steadily until 1914. The period 1914 to 1918 was one of rapid expansion as the natural gases of the Mid-Continent districts were treated. Since 1918 growth has been slower as a result of the fact that the gases that could be most profitably treated were being handled. Future growth will be slower, and will depend on the availability of new supplies of wet gases, and on the possible development of methods for more profitably treating the dry gases.

The volume of natural-gas gasoline produced annually is about 8 per cent of the total production of gasoline. But the natural-gas gasoline industry should be credited with making available not only this 8 per cent, but at least an additional 3 to 4 per cent of the total motor fuel supply, as a result of the practice of blending natural-gasoline with otherwise unsuitable naphthas and with gasolines.

The Distillation Range of Gasoline.

The broadening of the distillation range of gasoline has been the most important means by which the supply of motor fuel has been increased, other than the increase in production of crude oil. The U. S. Bureau of Mines made a limited investigation of the quality of gasoline in 1915, more extensive surveys in 1917 and in April, 1919, and since and including January, 1920, has made semi-annual reports on the quality of gasoline sold in the larger marketing centers.

Ten years ago gasoline was of 70° to 76° Bé. gravity, and distilled entirely under 300° to 350° F. The present Navy Specification calls for complete distillation under 437° F. Gasolines of today range from 54° to 60° Bé. gravity. This change in the boiling range of what is regarded as acceptable gasoline has allowed an increase of 50 to 75 per cent in the amount of gasoline distilled from most crude oils, and has thus been a factor of the greatest importance in increasing the motor fuel supply.

May a further broadening of the distillation range be expected? Possibly it is significant that in the two and one-half years prior to January, 1922, the quality of the gasolines examined by the U. S. Bureau of Mines has not changed appreciably. This entire subject is discussed in greater detail in Chapter XIV, and the main points only will be mentioned here. Further increase in the end point of gasoline may be checked until means are found to overcome inherent difficulties. The higher the average molecular weight of the gasoline hydrocarbons the more accurate the metering of gasoline and air must be, and as

general, the more complex the problems of carburetion. ceivable that these difficulties can be overcome. A furtl difficulty lies in the nature of the combustion process molecular weight hydrocarbons are introduced into the engi These phenomena have not been studied in sufficient detail a certain explanation at this time, but it appears at least p two concurrent chemical processes, thermal dissociation of carbons and oxidation or burning of both hydrocarbons position products, are involved. If the energy of the deton sion wave is increased by the oxidative reactions much moı decreased by the endothermic dissociations, the result will l travelling explosion wave that will cause a knock.[8] The hig weight hydrocarbons easily dissociate and decompose the therefore it is doubtful if much more high-boiling distil included in the hydrocarbon mixture marketed as gasoline u are provided for avoiding the knock.

The Distillation of Light Crude Oils.

The increased average yield of gasoline obtained from the refineries of the country has resulted in some measur use of crudes containing larger percentages of the more vol carbons. These crude oils came into the market as a re development of the great Mid-Continent field, and more the Northern Texas, Northern Louisiana, and Wyoming F the petroleum produced during recent years in Californi lighter than the crudes of the earlier days.

The more extensive use of light crudes cannot be r probable in the future, since approximately one-half of th reserve is in those regions that yield oil of low gasoline cont

The Development and Use of Cracking Processes.

Cracking processes are those processes of thermal de in which hydrocarbons of medium to high molecular weig verted into a variety of products, including lower molec hydrocarbons and higher molecular weight hydrocarbons. ing process that produces a maximum yield of gasoline of g with a minimum formation of gaseous and tarry substa most successful.

Several hundred patents have been granted in this cour foreign countries, covering methods or apparatus for the composition of oils. These may be roughly classed into t

1. Processes in which the oil in vapor form is therma getically treated.

2. Processes in which the oil is treated in liquid form.

The first class of processes is sometimes referred to

[8] T. Midgley, Jr., *Nat. Pet. News*, Jan. 12, 1921.

phase processes, and the second class, as liquid-phase processes. The processes of Greenstreet, Rittman, Alexander, General Petroleum Corporation, and Hall are examples of the vapor-phase method. The Burton process, the Cross process, and the pressure-still processes of the Sinclair Refining Company, and of Cosden and Company are examples of the liquid-phase method. In his address[9] of acceptance of the Perkin medal, Dr. Burton stated that the Burton stills operated by the Standard Oil Company of Indiana and its licensees produced two million gallons of gasoline daily. It is probable that 20 per cent of the gasoline marketed today is produced by cracking processes.

Cracking processes will be one of the important, if not the most important factor, in enabling the production of motor fuels to keep pace with demand. The cracking processes now in use handle the middle distillates such as gas oil. The urgent and apparent need is for processes that will treat the fuel oils and heavy asphaltic oils successfully. This need bids fair to be met in the near future, for at least one process is available that will handle heavy oils without the use of pressure. When the heavy oils are treated, middle-distillates are produced as well as gasoline. These distillates can be used as raw materials in either vapor-phase or pressure-still plants. Hence, as a result of the ability to crack residuum and fuel oils, a tremendous increase in the production of gasoline is made possible.

The subject of cracking processes is discussed in Chapter IX, to which reference should be made.

Aromatic Hydrocarbon Distillates.

The use of the lighter distillates from coal tar, or of these same hydrocarbons, benzene, toluene, and the xylenes, as they are scrubbed from coke oven or coal gases, has become of some importance. They may be used alone, but are preferably mixed with gasoline. Also they serve as useful blending agents in making composite fuels containing gasoline and alcohol.

Will the use of these substances be an important factor in the motor fuel situation A brief examination of statistics shows that too much must not be expected. In Table XII is shown the number of gallons[10] of the volatile aromatic distillates, i.e., benzene, toluene, xylenes, and solvent naphthas available.

The total production of aromatic distillates in 1918 equalled only 4.7 per cent of the total gasoline production of that year, and only 3.2 per cent of the gasoline production of 1921. These percentages are so small as to make it seem scarcely worth while to consider these distillates as motor fuels, particularly since a large demand for these products comes from other industries in which they are used as raw materials or as solvents. But in spite of this seeming unimportance

[9] *J. Ind. Eng. Chem.*, 14 (1922), 162-3.
[10] "Census of Dyes and Coal Tar Chemicals," 1919 Tariff Information Series —No. 11.

TABLE XII

PRODUCTION OF AROMATIC HYDROCARBON DISTILLATES IN THE UNITED STATES

[illegible]

Source	1917	1918
By-products from the manufacture of coke	[illegible]	[illegible]
By-products from coal gas plants	[illegible]	[illegible]
Products from coal tar distilleries	[illegible]	[illegible]
Other	[illegible]	[illegible]
Total	[illegible]	[illegible]

it will be found that several corporations will derive substantial returns from the sale of these products as fuels. So great is the total volume of motor fuels sold annually in this country that even 1 per cent of the total business is to be counted in millions of dollars.

The solution of the motor fuel problem will not be found in the use of aromatic distillates. This is obvious from the foregoing table considered in relation to the source of these fuels. The production of these distillates is largely dependent upon the scope of the by-product coking industry, and this in turn upon the steel industry. A healthy growth is to be expected, but nothing phenomenal or startling. The percentage of coal coked in by-product ovens and in gas plants will also increase. In 1918 the coal so handled was 40 per cent of the total coal coked, in 1920 60 per cent, and in 1921 over 75 per cent. The actual quantity of coal coked in 1921 was much less than in 1920 as a result of the business depression. Even with the continuance of present tendencies it seems hardly probable that over 3 per cent of the total motor fuel supply of the near future will consist of aromatic distillates.

The Possibility of a Shale Oil Industry.

High prices for petroleum, along with a growing recognition of the limitations of our oil reserve, have served to awaken interest in the commercial development of our great oil-shale resources. The U. S. Geological Survey has studied these deposits, particularly the rich shales of the Uinta Basin. Dean Winchester estimates[11] that the shale in the Utah portion of the Uinta Basin alone would yield 42,800,000,000 barrels of crude shale oil. He estimates[12] further that the shales of Colorado would yield 20,000,000,000 barrels of the crude oil. Dr. Victor Alderson[13] believes these latter shales are capable of producing 58,080,000,000 barrels of oil. These are figures beyond the limits of imagination, and for the present one may well be

[11] *U. S. Geol. Survey Bull. 691-B.*
[12] *U. S. Geol. Survey Bull. 641-F.*
[13] "The Oil-Shale Industry," p. 31.

satisfied with the knowledge that the oil shale resources of this country are enormous.

But to have and to utilize are two different matters. No large scale production of shale oil is now under way, though much experimentation in the laboratory, and in full sized retorts, has been carried out; and the Patent Office has taken up a new form of indoor sport in the shape of shale oil process applications.

Technical, economic, and social problems must be solved before shale oil can become an actuality on a large scale. Technically, the production of shale oil involves the cheap mining and handling of enormous quantities of shale, the retorting of the shale in such a way as to produce a maximum yield of oil of good quality, and finally the refining of the oil into gasoline, kerosene, distillates, lubricating oils, and fuel oil.

Economically, the development of a shale oil industry depends upon attracting large amounts of capital. The investment necessary for the production of a given volume of finished products will be larger than that necessary for the production of these products from petroleum. The interests to whom shale oils should appear most attractive are the western railroad companies that use oil for fuel.

From a combined economic and social standpoint, the development of the shale oil industry would necessitate the building of cities, and the evolution of new communities, in what are now barren and arid regions of the West. As Mr. Requa has pointed out, the mining of shale on a scale sufficiently large to produce a quantity of oil equal to the present output of petroleum would require the services of a labor army nearly equal to that now engaged in the mining of coal. This gives a truer picture of the size of the task than perhaps any other comparison, and shows at once that we cannot expect shale oil quickly to take the place of a failing supply of petroleum.

Alcohol as a Motor Fuel of the Future.

The value of ethyl alcohol as a motor fuel when used in admixture with gasoline or aromatic hydrocarbon distillates has been amply demonstrated. Alcohol and gasoline are not completely miscible, but the addition of blending agents such as benzene, or preferably small amounts of ether, renders them miscible. The composite motor fuels containing 30 to 40 per cent of alcohol, an equal or somewhat larger per cent of gasoline, along with smaller percentages of benzene and ether, can be vaporized by the ordinary carbureter and used in present type engines as satisfactorily, and probably more satisfactorily, than gasoline. The use of pure alcohol necessitates special engines with a high compression ratio. Without widespread facilities for the distribution of alcohol, the owner of a car using alcohol as fuel would always be inconvenienced. It is fortunate, therefore, that alcohol fuel mixtures have proved practical.

The manufacture of alcohol, and the availability of various raw

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Products from coal-tar distilleries	[illegible]	[illegible]
Other	[illegible]	[illegible]
Total	[illegible]	[illegible]

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The manufacture of alcohol, and the availability of various raw

materials, is discussed in Chapter XII. At this point it is sufficient to say that the use of food or feed stuffs in making alcohol in quantities sufficient to add largely to the motor fuel supply is quite out of the question. If alcohol is to be produced in large quantity, wood, or other cellulosic raw material, must be used. The integration and development of an alcohol industry based on cellulosic raw materials does not appear to be as serious a task as the development of a shale oil industry.

Engine Development.

Another solution, or part solution, of the motor fuel problem lies in the development of engines which will successfully utilize the heavier oils as fuel. Will the Diesel engine or the semi-Diesel engine be adapted to use on tractors, trucks, and possibly even on pleasure cars? This question is being studied, but as yet no definite trend is evident. May not the chemist do much to aid in the study of the problem? One of the chief obstacles to the use of heavy oil engines is their weight, necessitated by the excessive pressures within the cylinders. If the rate of combustion of the fuel could be increased by the use of catalysts, and the pressure necessary correspondingly decreased, a much lighter engine could be built. A limited amount of investigational work along this line has been done.

A further possibility lies in the building of explosion engines that will utilize the higher hydrocarbons without serious difficulty from knocking. The use of catalysts or chemical additions to the fuel may also have a bearing on this problem. The difficulty in burning kerosene is apparently related to the fact that two processes, combustion and thermal decomposition of the hydrocarbons, are taking place simultaneously in the cylinder. If the thermal decomposition could be inhibited, or the combustion brought about at lower temperatures, the difficulty would be avoided. Experimentation with catalysts is clearly suggested.

Finally we may inquire whether the steam-driven automobile has not been neglected. Would not the objections to the steam car be overcome by the application of even a small part of the energy and ingenuity that has been necessary for the development of the present asoline car. The steam car is far more flexible in operation than e gas car. No changing of gears is required. It is reasonable to ve that burners can be designed that will permit burning of heavy llates. And compared to difficulties that have been successfully come in the building of gasoline cars, the problem of developing itable and lasting boiler for the steam car is not formidable. Is it possible that our automotive engineers have been travelling in the of unintentional prejudice, formed as a result of their schooling experience in the years of development of the gasoline engine en car?

Whatever may be the outcome in the field of engine design and

development, some improvement may be expected in the direction of economy and utilization of heavier fuels. In this way the motor fuel problem may become somewhat less formidable than it now appears.

Summary.

The motor fuel problem is one of the great problems of the present day. The solution demands readjustment and development in the petroleum and related industries, and in the automotive industries.

The consumption of gasoline is now nearly five billion gallons annually, and may be expected to increase to at least seven billion gallons. Production of gasoline has kept pace with demand as a result of the increased production of crude oil, marketing of a gasoline of wider distillation range, the development of the natural-gas gasoline industry, the application of cracking processes, the blending of coal-tar distillates with gasoline, the importation of petroleum from foreign countries, and of the fact that petroleums distilled in recent years have contained a larger proportion of gasoline than those of ten years ago.

The United States produces two-thirds of the world's crude oil, but uses four-fifths of it. Our reserve supply below ground is about nine billion barrels, which, at a rate of production equal to that of 1921, would last only twenty years. We are now dependent upon foreign crude oils, and are importing more crude oil than our combined exports of petroleum and its products.

Great Britain now commands three-fourths of the oil reserves of the world. We must insist upon an open door policy on the part of other nations with regard to development of oil resources by our nationals. Our petroleum reserves are only 9 per cent of those of the entire world.

We cannot expect a further rapid expansion of the natural-gas gasoline industry, nor can the distillation range of gasoline be further materially increased. Chemical research must point the way toward success in utilization of the heavier distillates as motor fuels.

The problem of the transition from present sources of motor fuel to future sources will be solved by the development and use of cracking processes. The most important single technical problem is the cracking of the heavier 40 to 50 per cent of petroleum, the fuel oil or residuum. Processes now in use handle the middle distillates only.

The use of aromatic distillates as fuel will never be of more than minor importance.

Development of an alcohol industry may be anticipated. Shale oil is a distant possibility only. A noteworthy field of investigation is the study of the combustion process from a chemical standpoint, and important changes in the design of engines and accessory appliances may result. The much neglected steam car may receive the attention to which its advantages truly entitle it.

The motor fuel problem is one needing serious thought and constructive work on the part of individuals, corporations, and Government.

Chapter II.

The Composition of Petroleums.

Petroleums consist essentially of hydrocarbons of a few series, mixed with smaller amounts of substances composed mainly of carbon and hydrogen but also containing one or more of the elements oxygen, nitrogen, and sulfur. In some petroleums the hydrocarbons of one series predominate, while in others the hydrocarbons of two or more series are mixed in comparable proportions. The best known hydrocarbon series are those represented by the type formulas C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4}, and C_nH_{2n-6}. The heavier portions of some petroleums contain hydrocarbons less rich in hydrogen than the members of any of these series.

Many competent investigators have studied petroleums from various parts of the world in an effort to determine of what substances the oils are composed. The work is complicated by the extreme difficulty of isolating the chemical individuals, by the readiness with which the higher molecular weight substances decompose when heated above 360°C. at ordinary pressure, and by lack of such accurate knowledge of the chemistry and physical properties of the hydrocarbons as would result from careful study of synthetically prepared hydrocarbon substances. The investigations have, in the main, been carried out in the laboratories of the Universities. Because the value of the knowledge that might be obtained has not been, and possibly is not now, entirely apparent, the industry has not seen fit financially to support the extensive work that would be necessary to round out the field of petroleum chemistry. The result is that much that is done in the name of chemical engineering about an oil-refinery is little better than chemical "pipe-fitting." With the application of much imagination and moderate sums of money, it is entirely probable that results of as great value would be obtained as those in the field of iron and steel that are the result of the modern development of metallographical methods and constitutional theories.

The Origin of Petroleums.

Petroleums are formed from organic matter of vegetable or animal origin by a succession of chemical changes. This, at least, is the consensus of the opinion of those who have carefully studied the relationship of deposits of petroleum to the character of the fossil remains in the strata in which the oil is found. Additional evidence is found in

the fact that hydrocarbons similar to those in petroleum are formed when either plant or animal material is decomposed under proper experimental conditions. Furthermore, the ease with which the higher hydrocarbons are thermally decomposed precludes the possibility that petroleums were formed by any process involving temperatures higher than 360°C.

The relationship of some oil and coal deposits offers further positive evidence in support of the organic theory.[1]

The suggestion of Mendeleeff, later championed by Moissan, that the hydrocarbons of petroleum were formed from the products of the hydrolysis of carbides, now has few supporters. Nor is it generally believed that petroleums have been formed in one place, later to migrate long distances to the point where the commercial deposit is found. Movement over limited distance has no doubt occurred, as in the case of the Pennsylvania oils that have migrated transversely to the strata to lodge at different levels. In the event of such a movement the nature of the oil is changed in some measure by selective adsorption. Limited movements have, of course, been necessary to the collection of the oil in commercial deposits.

Dr. Mabery believes it evident that the petroleums consisting mainly of paraffin hydrocarbons have undergone less change in the process of formation than the oils containing naphthenes or asphaltic material. When sulfur is present in an oil, when the oil comes in contact with naturally occurring sulfur, or when sulfur is formed by the reduction of sulfates, the tendency is to form compounds that decompose with liberation of H_2S and simultaneous formation of asphaltic substances. Oxygen has similar effects.[2] The oils formed are poorer in hydrogen, higher in specific gravity, darker in color, and in some degree asphaltic in nature. The oils of Texas were probably formed in a manner similar to those of Pennsylvania, but came in contact with sulfur with the result that their chemical nature was changed at least in part.

Fundamental differences in the chemical nature of petroleums may also be ascribed to differences in the nature of the organic material from which the petroleums were derived. For a detailed review of the subject of the origin of petroleum reference should be made to standard works.[3]

Properties of Petroleum Hydrocarbons.

The paraffin hydrocarbons are chemically more stable than the hydrocarbons of the series less rich in hydrogen. With respect to

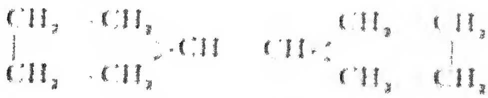
[1] White, David, *Wash. Acad. Sci.*, 5 (1915), 189; Mabery, *J. Ind. Eng. Chem.*, 6 (1914), 101-7.

[2] Mabery and Byerly, *Am. Chem. J.*, 18 (1886), 141. Kohler, H., "Die Chemie und Technologie der Naturlichen und Kunstlichen Asphalte." Rogers, G. S., U. S. Geol. Sur., *Bull. 623*, 1917, "Chemical Relations of Oil Field Waters," pp. 102-5.

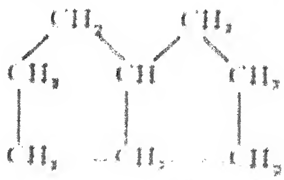
[3] Engler-Höfer, "Das Erdöl." Verlag von S. Hirzel, Leipzig, 1913. Redwood, "A Treatise on Petroleum." Chas. Griffin, London, 1922. Clarke, "The Data of Geochemistry." *U. S. Geol. Sur. Bull. No. 695* (1920).

thermal treatment the order of stability is the same. As the hydrog content becomes less, both thermal and chemical stability decrease pr gressively.

The structure of the paraffin, olefin, aromatic, and hexahydro ar matic hydrocarbons is well understood, but that of the series C_nH_{2n} and C_nH_{2n-4} and series still lower in hydrogen content is not co clusively known. The naphthene, or C_nH_{2n} compounds, are regard as of cyclic structure with various numbers of $-CH_2-$ groups the ring, and with saturated side chains. The C_nH_{2n-2} are probab either compounds containing two methylene rings joined by a bon between a carbon atom in each ring, or compounds with two comme carbon atoms. Examples of these are,



and



Saturated side chains are possible. Also the ring may not be saturate in which event the hydrocarbons of this series would be monocycli compounds with one double bond in the ring.

The C_nH_{2n-4} compounds may be of monocyclic ring structure wit two double bonds in the ring, or of bicyclic structure with union betwee two carbon atoms in each ring. Octohydronaphthalene is an exampl of the latter type. Reasoning from analogy with the reactions o naphthalene, this compound should yield phthalic acid on oxidation The observations of Dr. Mabery indicate that the oxidation of thes hydrocarbons results in the formation of products of lower molecula weight.

The lesser stability of the hydrocarbons that are poor in hydroge as compared to the paraffin hydrocarbons is illustrated by their lowe fire tests or greater ease of oxidation, and by their heats of formation If hydrocarbons of the C_nH_{2n+2} series are heated in a vacuum to 350° C and air is then allowed to enter, ignition and decomposition result If the hydrocarbons of the C_nH_{2n} are treated in a similar manner, th reaction ensuing is of explosive violence.

The thermal stability and reactions of the hydrocarbons are reviewed in detail in Chapter VIII. The chemical properties of the hydrocar bons are discussed in a limited way in connection with the various processes in relation to which the properties are of importance.

An extensive review of hydrocarbon chemistry is given in Engler-Höfer's "Das Erdöl." This, however, is a decade old. The most complete work on the subject is Dr. B. T. Brook's excellent recent book, "The Non-Benzenoid Hydrocarbons."

A Matter of View-point.

The discussion that follows will be limited in the main to the petroleums found in the United States. For a more extensive knowledge of the subject, reference must be made to larger works such as those just cited, and to the references given at the end of this chapter.

The subject of the composition of petroleum is usually presented by discussing each series of hydrocarbons, and then enumerating the petroleums in which these hydrocarbons have been found. The opposite method is followed here, that is, the composition of the petroleums of a chosen district is discussed. This, I hope, may give a clearer picture of the nature of the particular oils than is otherwise obtained.

The Composition of the Appalachian Petroleums.

The petroleums of Pennsylvania, Western New York, West Virginia, Eastern Ohio, and Eastern Kentucky are usually referred to as "paraffin-base" petroleums because of the fact that the hydrocarbons present in largest amount belong to the C_nH_{2n+2} or paraffin series. The cyclic hydrocarbons are present in much smaller amount, particularly in the lower boiling fractions of these petroleums. The lower molecular weight aromatic hydrocarbons and the olefins are present in minute quantities. The paraffin hydrocarbons are lacking in viscosity, and are therefore not valuable as lubricants. This is contrary to the popular misconception that the lubricating oils of highest quality are composed of paraffin hydrocarbons.

The light lubricating oils from the Appalachian petroleums are composed mainly of hydrocarbons of the series C_nH_{2n} and C_nH_{2n-2}. These are cyclic hydrocarbons, fully hydrogenated aromatic substances, called naphthenes by Markownikow, who discovered them in Russian oils. The more viscous hydrocarbons of the series C_nH_{2n-4} are present in small quantities only in the Appalachian petroleums. These oils, in contrast to most others, are almost free from sulfur, nitrogen, and oxygen compounds.

The Appalachian petroleums have been studied with great care by Mabery[a] and to some extent by Young.[b] The paraffins from butane C_4H_{10}, to pentatriacontane $C_{35}H_{72}$, the C_nH_{2n} series from $C_{21}H_{42}$ to $C_{26}H_{52}$, and $C_{27}H_{52}$ and $C_{28}H_{54}$ of the C_nH_{2n-2} series have been found by Mabery.

In addition to the paraffins, Young isolated the naphthenes pentamethylene, methyl-penta-methylene, hexamethylene, dimethyl-pentamethylene, and methyl-hexamethylene. Table XIII is a summary of the findings of Mabery and of Young.

[a] Mabery, *Econ. Geol.*, 11 (1916), 511-27; *J. Am. Chem. Soc.*, 28 (1906), 415-30; *Am. Chem. J.*, 18 (1896), 215; 19 (1897), 243 and 419; 28 (1902), 170. *Proc. Am. Acad. Sci.*, 31, 23; 32 (1897), 101-18, 121-76; 37 (1902), 565-95; 40 (1904), 346-62.

[b] Young, *J. Chem. Soc.*, 71 (1897), 440; 73 (1898), 904-20, 920-22, 922-28.

The paraffins of more than 14 carbon atoms are solids at ordinar
temperatures. The lower molecular weight C_nH_{2n} hydrocarbons ar
clearly monocyclic, but the structure of those of higher molecular weigl

TABLE XIII

HYDROCARBONS OF PENNSYLVANIA PETROLEUM

PARAFFIN HYDROCARBONS, C_nH_{2n+2}

Composition	Specific Gravity		Refractive Index	Boiling Point °C.	Pressure Mm. of Hg	Melting Point °C.	Observ
C_4H_{10} Iso				[illegible]	760 mm		Malery
C_5H_{12} Nor	.6263	[illegible]		36.3	"		Young
	.6401	0/4°					
	.6454	"					
" Iso	.6392	"		27.95	751 mm		"
C_6H_{14} Nor.	.6771	"		68.95	"		"
" Iso	.6710	"		61.00	"		"
C_7H_{16} Nor.				98.40	"		"
" Iso	.6969	0/4°		90.30	"		"
C_8H_{18} Nor	.7188	20/20°		125.00	760 mm		"
" Iso	.7190	"		119.50	"		Malery
C_9H_{20} Nor.				151.00	"		"
$C_{10}H_{22}$ "	.7479	"		162-164	"		"
" Iso	.7467	"		173-174	"		"
$C_{11}H_{24}$	.7581	"		196-197	"		"
$C_{12}H_{26}$ Nor	.7676	"		214-216	"		"
$C_{13}H_{28}$	.7834	"	1.451	226	"		"
$C_{14}H_{30}$	.7814	"	1.436	236-238	"		"
$C_{15}H_{32}$	.7896	"	1.4413	256-257	"		"
$C_{16}H_{34}$	.7911	"	1.4413	274-275	"		"
$C_{17}H_{36}$	.8000	"	1.4435	288-289	"	10	"
$C_{18}H_{38}$	.8017	"	1.440	300-301	"	20	"
$C_{19}H_{40}$	.8122	"	1.4522	210-212	50 mm	33-34	"
$C_{20}H_{42}$				230-231	"	40-41	"
$C_{21}H_{44}$	.7796	15°		240-242	"	44	"
$C_{22}H_{46}$	.7900	60		258-261	"	45	"
$C_{23}H_{48}$	.7902	"		272-274	"	48	"
$C_{24}H_{50}$	.7941	"		280-282	"	53-54	"
$C_{25}H_{52}$	.7977	"		292-294	"	58	"
$C_{26}H_{54}$	.7945	70		310-312	"	60	"
$C_{27}H_{56}$	.7992	"		328-330	"	66	"
$C_{28}H_{58}$	.8005	75		342-345	"	68	"
$C_{29}H_{60}$	.8009	80		366-368	"	72	"
$C_{30}H_{62}$	.80052	"		380-384	"	76	"

MONOCYCLIC POLYMETHYLENES, C_nH_{2n}

Composition	Specific Gravity		Boiling Point	Pressure	Observe
C_5H_{10} Penta-methylene	.7000	0/4°	50°	760 mm.	Young
C_6H_{12} Methyl-penta-methylene	.7660	"	72	"	"
C_6H_{12} Hexamethylene	.7722	"	80.6	"	"
C_7H_{14} Dimethyl-penta-methylene	.7543	20/4°	94	"	"
C_7H_{14} Methyl-hexamethylene	.7964		102	"	"

TABLE XIII—*Continued*

HYDROCARBONS, C_nH_{2n}

Composition	Specific Gravity	Refractive Index	Boiling Point	Pressure	Observer
$C_{21}H_{42}$	.8424 20/20°				
$C_{22}H_{44}$	.8262 "	1.454	240–242°	50 mm.	Malbery
$C_{23}H_{46}$	.8569 "	1.4714	258–260	" "	"
$C_{24}H_{48}$	.8598 "	1.4726	272–274	" "	"
$C_{26}H_{52}$	.8580 "	1.4725	280–282	" "	"

HYDROCARBONS, C_nH_{2n-2}

Composition	Specific Gravity	Refractive Index	Boiling Point	Pressure	Observer
$C_{27}H_{52}$	.8688 20/20°	1.4722	290–294°	50 mm.	Malbery
$C_{28}H_{54}$	.8694 "	1.4800	310–312	" "	"

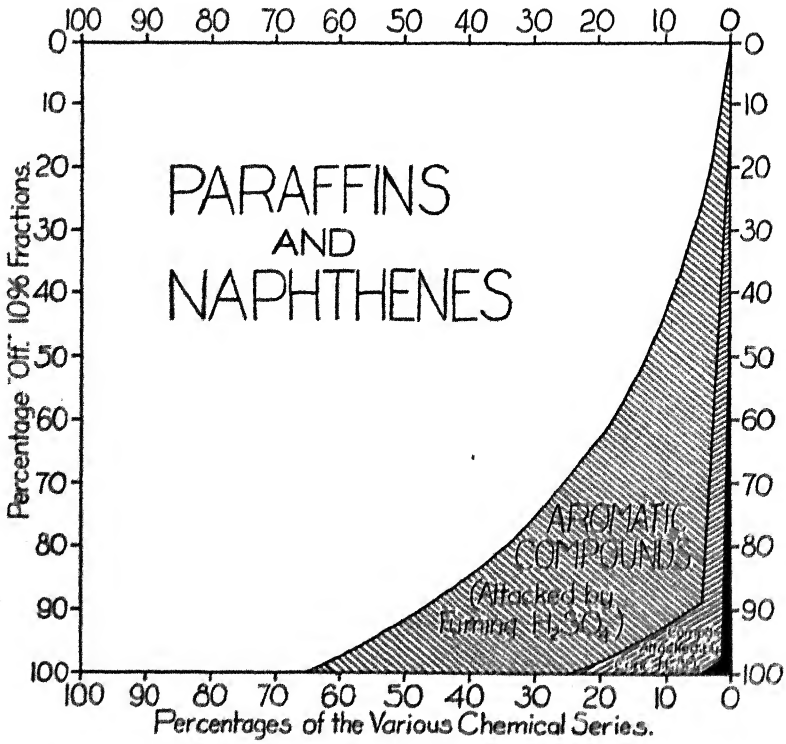


FIG. 5.—Diagram of Components of a Paraffin-Base Petroleum.

cannot be stated. They are different from the hydrocarbons of the same specific gravity and refractive index obtained from asphaltic oils. For instance, they boil 100° C. higher, and they do not react readily with concentrated sulfuric acid.

The heavy still residues from Pennsylvania petroleum have been studied by Richardson,[6] who found that over half of it consisted of solid paraffins. One-tenth to one-fifth of the residue was soluble in concentrated sulfuric acid.

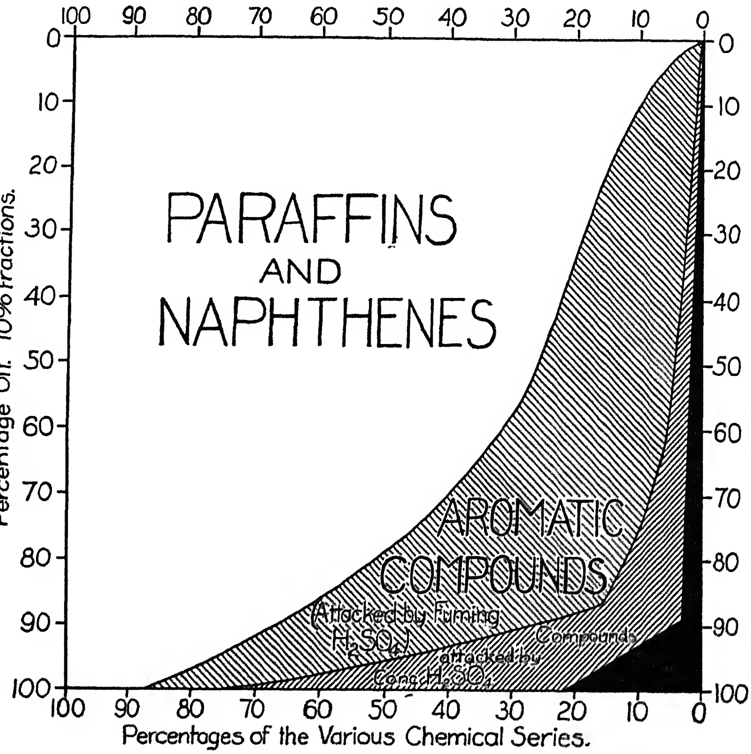


FIG. 6.—Diagram of Components of an Illinois Petroleum.

The composition of a Pennsylvania oil, an Illinois oil, and a heavy ʰaltic oil are shown in comparison in Figures[7] 5, 6, and 7. The represents the black asphaltic material that can be removed tive filtration. The significance of the other shadings is in the diagrams. The separations of the several chemical ⁿeans of sulfuric acid is not as definite as the delineation of s, but an interesting comparison of at least a qualitative

[6] Richardson, *J. Fr. Inst.*, 162 (1906), 57-70.
[7] F. C. Robinson, *Chem. Met. Eng.*, 11 (1913), 389-94.

nature is afforded. It should be noted that the figures are so constructed as to give the proportions of the several type components for each part of the oil from lowest boiling to highest boiling.

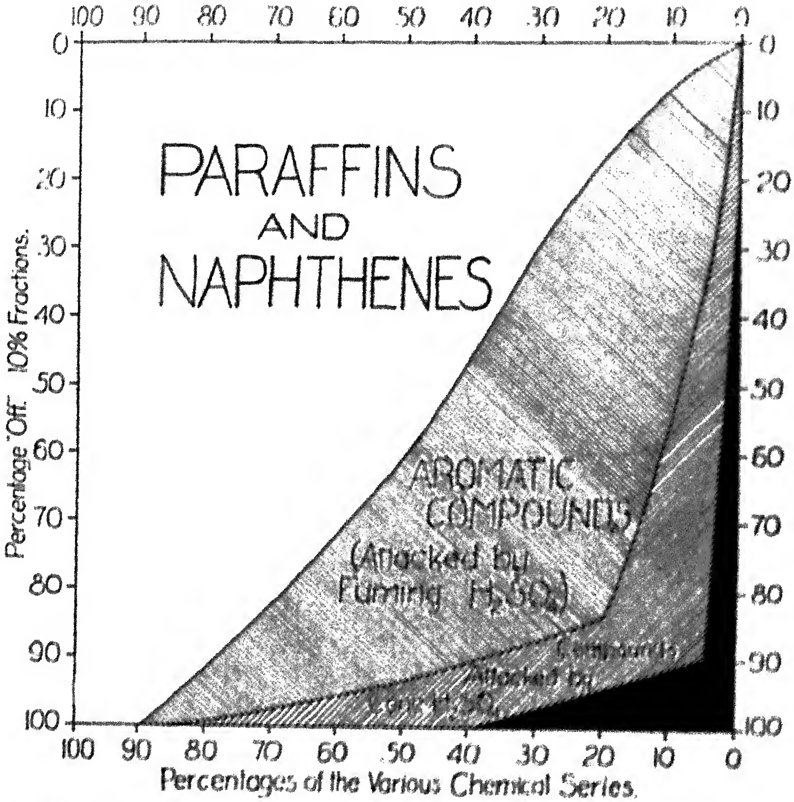


FIG. 7.—Diagram of Components of an Asphalt-Base Petroleum.

The Composition of Trenton and Canadian Corniferous Petroleums.

These petroleums are not of great importance today, but are of interest because their discovery necessitated the development of processes for refining oils containing sulfur compounds. The proportion of paraffin hydrocarbons is less, and that of the aromatic hydrocarbons, saturated C_nH_{2n}, and C_nH_{2n-2} hydrocarbons, greater, in these oils than in the Appalachian petroleums. Sulfur is present in the Ohio oils in amounts up to 0.5 per cent, and in the Canadian oils up to 1.0 per cent. The paraffins up to $C_{11}H_{24}$, the C_nH_{2n} series from $C_{10}H_{20}$ to [illegible], the C_nH_{2n-2} series from $C_{19}H_{36}$ to $C_{22}H_{42}$, and the series C_nH_{2n-4} from $C_{23}H_{42}$ to $C_{25}H_{46}$ were found in the Trenton oils of Ohio. The higher

molecular weight solid paraffins are also present in quantity. The papers of Mabery[8] should be consulted for further details.

Composition of Mahone Petroleum.

The petroleum from Mahoning County, Ohio, has been carefully studied by Mabery.[9] While this petroleum is not of great commercial importance, the work on its composition is important because it adds one more chapter to our knowledge of the chemistry of heavy oils. The crude petroleum is nearly black in color, and of 0.9042 specific gravity. Examination showed that none of the paraffin or C_nH_{2n} hydrocarbons were present. The C_nH_{2n-2} hydrocarbons from $C_{11}H_{20}$ to $C_{15}H_{28}$ were present in moderate amount. But the oil consisted mainly of the C_nH_{2n-4} hydrocarbons $C_{16}H_{28}$, $C_{17}H_{30}$ and $C_{19}H_{34}$. Thus the commercial lubricants made from this oil are composed largely of two or three hydrocarbons. The valuable lubricants from the heavy California, Texas, and Louisiana oil also consist mainly of C_nH_{2n-4} hydrocarbons.

An interesting feature, and one that distinguishes the heavy Mahone petroleum from other heavy oils is the low per cent of sulfur (0.01 per cent), and the absence of nitrogen.

The Composition of California and Gulf Coast Petroleums.

The series C_nH_{2n-2}, the hydrocarbons of which compose the larger part of the Appalachian petroleums, is completely wanting in the heavy petroleums of California and the Gulf Coast. The hydrocarbons of these oils contain less hydrogen than the paraffins, and those of moderate to high molecular weight decompose readily when distilled. The presence of air results in more extensive decomposition. The aromatic hydrocarbons are present in moderate quantity in some of these oils. Sulfur, nitrogen, and oxygen compounds are present in moderate to large amount. Mabery reports that no solid paraffins have been found in these heavy oils, but that crystals separated from the 275° to 295° C. fraction of Torrey Canyon oil that melted at 57° C. These high melting crystalline hydrocarbons are now separated from some California oils.

In 1897 Mabery[10] reported the results of an examination of those fractions of an oil from Ventura, California, boiling below 175° C. The aromatic hydrocarbons were present in moderate quantity, but the chief components were the methylenes. This was the first time that these hydrocarbons had been recognized in American petroleum.

The examination of California oils from the Ventura, Coalinga, Puente Hills, and Summerland fields are also recorded by Mabery.[11]

[8] *Proc. Amer. Acad. of Sci.*, 31 (1896), 1-65; 32 (1897), 143-76; 40 (1904), 323-40. *Amer. Chem. J.*, 13 (1891), 89; 19 (1897), 419; 33 (1905), 251.

[9] *J. Ind. Eng. Chem.*, 6 (1914), 101-7.

[10] *Am. Chem. J.*, 19 (1897), 796.

[11] *Proc. Am. Acad. Arts & Sci.*, 36 (1901), 255-95.

The Fresno oil from Coalinga was found to contain the hydrocarbons shown in Table XIV.

TABLE XIV

HYDROCARBONS OF A COALINGA, CALIFORNIA, PETROLEUM

Name	Boiling Point °C.	Specific Gravity at 20° C.	Comp. of Distillate Per Cent	
			Carbon	Hydrogen
Hexane C_6H_{14}	68–70	Mixed Fraction 0.6844	84.4	15.3
Hexamethylene C_6H_{12}	68–70			
Heptamethylene C_7H_{14}	96–98	0.7413	85.74	14.35
Benzene C_6H_6 *	79–81	.....	....	....
Toluene C_7H_8 **	109–110	.....	....	....
Octonaphthene C_8H_{16}	118–120	0.7532	85.36	14.98
Nononaphthene C_9H_{18}	134–135	0.7591	85.21	14.68
Xylenes C_8H_{10} ***	137–140	.....	....	....
Dekanaphthene $C_{10}H_{20}$	160–161	0.7840	85.55	14.50
Undekanaphthene $C_{11}H_{22}$	188–191	0.8044	85.70	14.40
Dodekonaphthene $C_{12}H_{24}$	208–210	.....	85.26	14.57

* One-third of the distillate collecting at this temperature was benzene.
** Over one-half of the distillate collecting at this temperature was toluene.
*** Three-fifths of the distillate collecting at this temperature was xylenes.

The hexane from the fraction boiling at 68°-70° C. is the highest boiling paraffin separated from the oil. Small quantities of distillates collected in the vicinity of 30°, 38° and 60° C., indicating that the most volatil material in the oil was composed of paraffins.

The fractions boiling at 160 to 161°, 169 to 170°, and 188 to 191° C. were largely composed of higher aromatic hydrocarbons, the naphthenes shown in Table XIV constituting the smaller part of these fractions. The higher boiling portion of this oil was not examined. (Specific gravity 0.892 at 20° C., Sulfur 0.8 per cent, N 1.2 per cent.)

The Puente oil was found to contain the naphthenes C_7H_{14}, C_8H_{16}, $C_{10}H_{20}$, $C_{11}H_{22}$. The paraffins boiling above 95° C. were absent. Aromatic hydrocarbons were present in quantity, particularly in the fraction boiling at 168 to 172° C. That part of the oil boiling above 200° C. was not examined.

The Bardsdale, Adams Canyon, Torrey Wells, and Scott's Hill (Sespe District), were similar, in a qualitative way at least, to the Coalinga and Puente oils. The naphthenes $C_{13}H_{26}$, $C_{14}H_{28}$ and $C_{15}H_{30}$ were isolated from the Scott's Hill Oil.

Dr. Mabery summarizes his work on these oils as follows:

"An essential characteristic is the relatively small proportion of the distillates below 225° C. The main body of the crude oils from the principal fields distilling below 225° C. is composed of methylenes which resemble those identified in Russian oil, in boiling points and in specific gravity, except undekanaphthene $C_{11}H_{22}$, dodekanaphthene $C_{12}H_{24}$, and tridekanaphthene $C_{13}H_{26}$, which differ in boiling points.

The proportion of the aromatic hydrocarbons is much larger, apparently, in California oil. The homologues of benzene form a considerable proportion of the distillates, especially those with lower boiling points. In the distillate 221 to 222° C. from Puente oil so much naphthalene was present that the distillate became solid at 0° C.

"California petroleum differs totally from the Eastern oils—Pennsylvania, Ohio, Canadian, etc.,—and also materially from Russian oil, in not containing members of the series C_nH_{2n+2}. In this respect, and in respect to the large proportion of aromatic hydrocarbons, California petroleum is unlike any other petroleum that has been examined in this laboratory."

Mabery's[12] examination of the petroleum from the Summerland field in California is important because of the fact that the higher boiling fractions of the oil were studied. The oil was very heavy (specific gravity 0.9845 at 20° C.), and contained 0.84 per cent sulfur and 1.25 per cent nitrogen. None of the oil distilled below 200° C. at atmospheric pressure. The distillations were made under a vacuum of 60 mm. The investigation, the results of which are shown in Table XV, showed that the lower boiling hydrocarbons belonged to the series C_nH_{2n-2} and the higher boiling to series whose members contain less hydrogen. Members of the series C_nH_{2n-8} were identified.

TABLE XV

HYDROCARBONS OF SUMMERLAND, CALIFORNIA, PETROLEUM

Hydrocarbon Series	Formula	Boiling Point at 60 mm. °C.	Specific Gravity at 20° C.
C_nH_{2n-2}	$C_{13}H_{24}$	150–155	0.8621
"	$C_{16}H_{30}$	175–180	0.8808
C_nH_{2n-4}	$C_{17}H_{30}$	190–195	0.8919
"	$C_{18}H_{32}$	210–215	0.8996
"	$C_{24}H_{44}$	250–255	0.9299
C_nH_{2n-8}	$C_{27}H_{46}$	310–315	0.9451
"	$C_{29}H_{50}$	340–345	0.9778

Some California petroleums according to Engler-Höfer have higher nitrogen (2.4 per cent) contents than any other crude oils. Japanese and Algerian petroleums both contain over 2.0 per cent of nitrogen, but in general the nitrogen content of petroleums is well under 1.5 per cent. The nature of the nitrogen compounds of California oil is discussed in a later section.

A heavy oil from Jefferson County, Texas, was examined by Mabery[13] and Buck. The specific gravity was 0.950, and the sulfur content 0.94 per cent. None of the oil distilled below 240° C. Chemical examination showed that it consisted of the hydrocarbons $C_{14}H_{26}$ to $C_{19}H_{36}$ of the series C_nH_{2n-2}, and $C_{21}H_{38}$ to $C_{25}H_{46}$ of the series

[12] *Proc. Am. Acad. Arts & Sci.*, 40 (1904), 340-46.
[13] *J. Am. Chem. Soc.*, 22 (1900), 553-56.

C_nH_{2n-4}. These were believed to be bicyclic methylenes. The properties of these hydrocarbons are shown in Table XVI.

TABLE XVI

Properties of Hydrocarbons of Petroleum from Jefferson Co., Texas

Hydrocarbon	Boiling Point at 25 mm. °C.	Specific Gravity	Index of Refraction	Molecular Refraction	
				Calculated	Found
$C_{14}H_{26}$	125–130	0.8711	1.4713	62.34	62.39
$C_{15}H_{28}$	140–145	0.8788	1.4746	66.94	66.70
$C_{16}H_{30}$	160–165	0.8894	1.4672	71.55	69.40
$C_{17}H_{32}$	175–180	0.8966	1.4721	76.14	73.85
$C_{19}H_{36}$	195–200	0.9020	1.4928	85.35	84.70
$C_{21}H_{38}$	215–220	0.9163	1.4979	92.46	92.91
$C_{25}H_{46}$	270–275	0.9410	1.5152	110.87	111.00

The petroleum from the famous Lucas well on Spindle Top, near Beaumont, was examined by Mabery.[14] The specific gravity of the oil was 0.920, and the sulfur content was 2.16 per cent (including H_2S). It also contained over 1 per cent of nitrogen. The principal series of hydrocarbons in this oil was found to be C_nH_{2n-2}, of which the members $C_{12}H_{22}$, $C_{14}H_{26}$, $C_{16}H_{30}$ were found. Since the hydrocarbons showed no evidence of unsaturation Mabery believed them to be of a structure similar to dihexahydro-diphenyl.

$$H_2C<\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}>CH-CH<\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}>CH_2$$

The hydrocarbons of higher molecular weight might contain this same bicyclic nucleus with alkyl groups substituted for one or more of the hydrogens. The sulfur compounds of the heavy Texas oil are less stable than those of the Lima, Ohio, petroleums.

C. Richardson[15] has also examined petroleum from Beaumont, Texas. He concluded that the oil was composed largely of bicyclic polymethylenes along with smaller amounts of unsaturated hydrocarbons and their sulfur derivatives. The sulfur compounds are adsorbed during filtration through 60 mesh clay. On standing, the heavier portions that passed through the clay filter deposited regular crystals of sulfur equal in weight to 0.25 per cent of the oil.

The composition of Louisiana petroleum from the Jennings field has been studied by C. E. Coates.[16] The lowest member of the C_nH_{2-2} series then known was $C_{12}H_{22}$. Coates does not agree with Mabery's suggestion that this hydrocarbon was dihexahydrodiphenyl and that the other members of the series were its homologues, since he isolated a hydrocarbon, $C_{11}H_{20}$, which could not contain two six-membered

[14] *J. Am. Chem. Soc.*, 23 (1901), 264-67.
[15] *J. Soc. Chem. Ind.*, 20 (1901), 690; 21 (1902), 316.
[16] *J. Am. Chem. Soc.*, 28 (1906), 384-88; 25 (1903), 1153-58.

rings. The lightest hydrocarbons of the Jenning's oil were found to be $C_{10}H_{18}$, $C_{11}H_{20}$, $C_{12}H_{22}$, and $C_{13}H_{24}$. These decomposed very readily during distillation at ordinary pressure, and to some extent at 16 mm. pressure. None of the hydrocarbons absorbed iodine or bromine, according to Coates, nor did the molecular refraction indicate the presence of double bonds. A bicyclic structure of some sort was regarded as most probable.

The Composition of Mid-Continent Petroleums.

The oil fields of Kansas, Oklahoma, Northern Louisiana, and Texas have been developed more recently than those of the Appalachian, Gulf Coast, and Californian regions. Despite their tremendous importance, little has been done in the way of determining the chemical composition of these petroleums. Even superficial examination indicates that oils from various fields in the Mid-Continent differ greatly in composition. They possess, in varying degree, the properties of both the paraffin-base and asphaltic oils, and are therefore frequently referred to as mixed-base petroleums.

F. W. Bushong[17] reports the physical characteristics of several Kansas oils, and gives analyses for sulfur. The same author reports an investigation[18] of an Oklahoma oil in which the elementary composition of some of the fractions was determined and the nature of certain ozonides studied.

Brooks and Humphrey[19] believe that the formation of aromatic hydrocarbons from Mid-Continent oils when cracked is to be ascribed to the presence of benzene homologues in the oils.

Sulfur Compounds in Petroleums.

Sulfur is the most undesirable impurity present in petroleums. It is found in nearly all oils, though the amount in the Appalachian [illegible] is negligible. Mabery[20] states that samples of Humble crude, with a 2.75 per cent sulfur content, contained more sulfur than any other oil he has examined. Sulfur was first observed in the oils of Petrolia, Canada, which contained about 1 per cent, next in the Lima, Ohio, oils during the late eighties, and more recently in the oils of California, Illinois, the Gulf Coast, Kansas, Louisiana, Texas, and Wyoming. The presence of sulfur in petroleums is ascribed to the formation of the oil from organic matter containing sulfur, to contact with naturally occurring beds of sulfur, or to reduction of sulfates in the ground waters.

Ordinarily sulfur is present in combination, but in some oils, as, for example, those from the Gulf Coast, free sulfur is found. This

[17] *Univ. Geol. Sur. Kansas*, 9 (1908), 303-17.
[18] *J. Ind. Eng. Chem.*, 6 (1914), 888.
[19] *J. Am. Chem. Soc.*, 38 (1916), 393-400.
[20] *Bull. Am. Inst. Min. Met. Eng.*, 65 (1920), 505-21.

has already been referred to in the discussion of the composition of these oils.

The nature of the sulfur compounds in the Canadian petroleum as found by Mabery[21] is of interest. It has been shown that they are neither mercaptans nor thiophenes. The sulfur compounds from Ohio petroleum formed crystalline addition products with alcoholic mercuric chloride, and the sulfur oils resembled alkyl sulfides. The compounds, of somewhat higher boiling point, in Canadian oils are not alkyl sulfides, mercaptans, thiophenes, or ethylene sulfides. Their high specific gravity shows that they belong to a new series whose members are termed thiophanes by Mabery. Empirically, they are hydrothiophenes with long side chains, methylene sulfides with numerous, or long, side chains, or simple ring methylene sulfides. A condensed ring structure is excluded because the empirical composition of the compounds is $C_nH_{2n}S$. The general structure is probably of the type

$$\begin{array}{l} H_2C - CH_2 - CH_2 \\ \;\;\;| \qquad\qquad\qquad > S \\ H_2C - CH_2 - CH_2 \end{array}$$

The hydrogens may be replaced by side chains. The rings are probably of few carbon atoms. When the structure of the C_nH_{2n}, C_nH_{2n-2}, and C_nH_{2n-4} hydrocarbons of petroleum is further elucidated, the structure of the sulfides will probably be more easily understood.

The thiophanes isolated from Canadian petroleum are:

	Boiling Point °C.
Hexylthiophane $C_6H_{12}S$	125–130
Heptylthiophane $C_7H_{14}S$....................	158–160
Octylthiophane $C_8H_{16}S$	168
Nonylthiophane $C_9H_{18}S$	193
Decylthiophane $C_{10}H_{20}S$	208
Octdecylthiophane $C_{18}H_{36}S$	290–295

The alkyl sulfides from Canadian petroleum, and the boiling point of the fraction of the oil from which the sulfide was isolated are:

	Boiling Point of Petroleum Fractions °C.
Methyl Sulfide $(CH_3)_2S$	100–120
Ethyl Sulfide $(C_2H_5)_2S$	135–140
Isobutyl Sulfide $(C_4H_{10})_2S$	156–160
Pentyl Sulfide $(C_5H_{12})_2S$	205–210
Hexyl Sulfide $(C_6H_{14})_2S$	225–235

[21] *Am. Chem. J.*, 13 (1891), 232; 16 (1894), 83-93. *Proc. Amer. Acad. Sci.*, 41 (1905), 89-113.

Perkin,[22] in a paper on sulfur in petroleum oils, notes that thiophene, C_4H_4S, has been found in small quantity in Russian and German oils. A list of thiophenes, together with the boiling points and specific gravities, is given, and is here reproduced.

	Boiling Point °C.	Specific Gravity
Thiophene C_4H_4S	84	1.09
Methylthiophene C_5H_6S	112	.....
Ethylthiophene C_6H_8S	133	0.99
Dimethylthiophene C_6H_8S	137	0.994
Propylthiophene $C_7H_{10}S$	157	0.974
Octylthiophene $C_{12}H_{20}S$	258	0.812

The work of Meyer and Nahnsen,[23] who found that thiophene was formed in small quantities when a mixture of benzene and petroleum vapor was passed over strongly heated pyrites, is referred to by Perkin as of possible interest in connection with the formation of the sulfur compounds in petroleum. Friedman [24] heated normal octane in a sealed tube with sulfur to 270 to 280° C., and found that a thiophane $C_8H_{12}S$, a thiophene $C_8H_8S_2$, and H_2S were formed. The same compounds were produced when octylene was heated with sulfur, except that no H_2S was formed.

When one considers the large number of possible sulfur compounds and the diversity of their boiling points, it is not surprising that sulfur is found in petroleum distillates of all boiling points. As a rule, the sulfur content of the fractions from any oil increases with rise in boiling point. Perkin cites an analysis of the fractions from an "American" petroleum containing 0.72 per cent sulfur:

Fraction	Sulfur Per Cent	Specific Gravity
to 90°C.	0.02	......
110–150	0.10	0.7282
150–220	0.38	0.7669
220–257	0.41	0.7940
257–300	0.37	0.8138
300–350	0.37	0.8242
Residue	0.54	0.8976

Apparently some of the sulfur was removed by splitting off H_2S during distillation, since the average content of the fractions is less than that of the original oil.

Nitrogen in Petroleums.

The presence of nitrogen compounds in petroleum has long been recognized, but little is known of their chemical nature. Pyridine and

[22] *J. Inst. Pet. Tech.*, 3 (1917), 227-50.
[23] *Ber.*, 18, 217.
[24] *Ber.*, 49 (1916), 1344.

its homologues have been reported as present in some European petroleums, but an examination of American and of Baku petroleums indicated, according to Dr. Mabery, that the nitrogen compounds of these oils are not pyridine derivatives. Peckham[25] noted the presence of nitrogen bases in California petroleum.

The nature of the nitrogen compounds that compose as much as 20 per cent of some California petroleums has been studied by Mabery.[26] Petroleum from Santa Paula, California, was found to contain substances of the following composition:

Boiling Point of Fraction at 50–90 mm.	Formula
130–140° C.	$C_{12}H_{17}N$
197–199	$C_{13}H_{18}N$
209–211	$C_{14}H_{19}N$
215–217	$C_{15}H_{19}N$
223–225	$C_{16}H_{19}N$
270–275	$C_{17}H_{21}N$

Present knowledge of the nitrogen compounds of petroleum is summarized by Mabery as follows:

"They form illy-defined precipitates from acid solution with platinum, palladium, mercuric, cadmium, and ferric chlorides, potassium dichromate, ferro- and ferri-cyanides, and picric and oxalic acids. By oxidation with potassium permanganate in alkaline solutions the nitrogen of the bases is evolved in part as ammonia and in part as free nitrogen. Oxidation with chromic acid forms free nitrogen, and, in some cases, a small amount of acetic acid. Ethyl iodide adds to the bases if heated with them in a sealed tube. The bases are volatile with steam; they have an odor variously described as 'pyridine-,' 'quinoline-' or 'nicotine-like'; they possess rather weakly basic qualities; and, while nearly immiscible with water, they dissolve readily in alcohol, ether, benzene, and carbon-disulfide."

Mabery's later work shows that careful oxidation of the nitrogen compounds from Santa Paula, California, petroleum yields pyridine tetracarboxylic acid and methyl-pyridine tetracarboxylic acid. Traces only of the aliphatic acids were formed, and the acids composing this minute quantity were of lower molecular weight than butyric. Oxidation of one of the fractions with chromic acid, followed by distillation of the calcium salts of the acids so formed, gave β-methyl quinoline.

The nitrogen bases can be reduced with alcohol and sodium amalgam, by tin and HCl, or by hydroiodic acid at 290 to 300° C. The nitrogen atom of the hydrogenated nucleus is then present as a secondary, rather than a tertiary, base. The elementary composition of two carefully purified fractions corresponded to that of the alkylated quinolines or iso-quinolines. The behavior of the bases was not contrary to that which would be expected of highly alkylated quinolines or iso-quinolines.

[25] *Am. J. Sci.,* 48 (3), (1894), 250.
[26] *J. Soc. Chem. Ind.,* 19 (1900), 505. *J. Am. Chem. Soc.,* 42 (1920), 1014-30.

Mabery concludes that the nitrogen bases of California petroleum consist mainly of an indefinite mixture of alkylated quinolines or iso-quinolines, which, as regards the nitrogen-containing ring are completely alkylated. The alkyl side-chains are short, that is, groups such as methyl, ethyl, or propyl. In the compound $C_{12}H_{13}N$ the three side chains must be methyl groups. The previous difficulty in identifying these comparatively simple nitrogen compounds, by the preparation of salts such as chloroplatinates, is the result of the fact that each fraction is a mixture of bases. Existence in this form prevents the crystallization of salts of the bases as well as the bases themselves. The admixture of 10 per cent of isomers or homologues of a base, with 90 per cent of the pure base, gives a mixture from which salts, pure enough for identification, cannot be separated.

Additional references on nitrogen compounds will be found in the list at the end of this chapter.

Oxygen Compounds in Petroleum.

Most petroleums contain some oxygen compounds, usually in the form of naphthene carboxylic acid or phenols. Mabery [27] has reported the finding of phenolic substances in California petroleum. Most of the work on the oxygen compounds of petroleum has been carried out in Europe. Markownikow,[28] while studying the nature of the components of Caucasian petroleum, isolated acidic compounds, one of which was identical with that previously isolated by Hell and Medinger.[29] He considered these compounds naphthene mono-carboxylic acids, and was confirmed in this conclusion by Aschan, who converted octonaphthenic acid $C_8H_{14}O_2$ into the corresponding amide, and this into the nitrile $C_7H_{13}CN$, or into the amine $C_7H_{18}NH_2$. Reduction with hydroiodic acid and phosphorus converted the acid into an octonaphthene identical with that found in petroleum.

Reviews of the subject of oxygen compounds in petroleum are given by Redwood,[30] by G. S. Rogers,[31] and by F. W. Bushong.[32]

Ultimate Analyses of Petroleums.

Ultimate analyses of American petroleums are shown in Table XVII.

[27] *J. Am. Chem. Soc.*, 28 (1906), 596.
[28] *Ann. de chim. et de Phys.*, 2 (6), (1884), 372. *J. Prakt. Chem.*, 49 (2), (1894), 88.
[29] *Ber.*, 7 (1874), 1216; 10 (1877), 541.
[30] "A Treatise on Petroleum" (1922), Vol. I, pp. 322-25.
[31] *U. S. Geol. Sur., Bull. 653* (1917), 102-5.
[32] 8th Int. Cong. App. Chem., 6, 57.

TABLE XVII

ULTIMATE ANALYSES OF PETROLEUMS

APPALACHIAN PETROLEUMS

Source of the Oil	Specific Gravity	Per Cent C	H	O	S	N	Observer and Reference
West Virginia — Rogers Gulch	0.857	83.2	13.2	3.6	....	....	H. St. Clair, Deville. *Compt. Rend.*, 66, 442, 453; 68, 349, 485, 686; 69, 933. *Ding. Poly. J.*, 189, 50; 192, 204; 193, 61, 124; 195, 209. *Jahr. Chem.*, 1868, 975; 1869, 1126.
West Virginia—Mecook	0.897	83.6	12.9	3.5	....	....	
West Virginia — Burning Springs	0.841	84.3	14.1	1.6	....	....	
Pennsylvania—Oil Creek	0.816	82.0	14.8	3.2	....	....	
Pennsylvania—Allegheny	0.866	84.9	13.7	1.4	....	....	
Ohio	0.887	84.2	13.1	2.7	....	....	S. F. Peckham—*Rep. Geol. Sur.*, 2, 89.
West Virginia — Cumberland	.....	85.2	13.4	...	....	0.54	
Ohio, Mecca	.....	86.3	13.1	...	....	0.23	
Lima, Ohio	.....	85.0	13.8	...	0.60	....	Rakusin, "Unt. das Erdöls," p. 78.
Findlay, Ohio	0.836	84.6	13.6	...	0.72	0.11	Mabery, *Am. Chem. J.*, 17, 713.
Pennsylvania, Oil City	0.8095	85.8	14.0	...	....	0.06	18, 55, 149, 165.
Pennsylvania	.....	86.1	13.9	...	0.06	....	Engler, *Ber.* 28, 2501.
CALIFORNIA, GULF COAST, AND MEXICAN PETROLEUMS							
California—Ventura	......	86.9	11.8	..	....	1.11	S. F. Peckham, *Rep. Geol. Sur.*, 2, 89.
California—Ventura	......	84.0	12.7	..	0.40	1.70	*U. S. Geol. Sur., 18th Ann. Rep.*, 1896-97, 842.
California—McKittrick	......	86.1	11.45	..	0.87	....	O'Neill, *J. Am. Chem. Soc.*, 25, 699.
California—Summerland	0.9845 at 20° C.	86.3	11.7	..	0.84	1.25	Mabery, *Proc. Am. Acad. Arts & Sci.*, 40 (1904), 341.
California—Puente	0.892 at 20°	85.0	12.0	..	0.8	1.2	Mabery, *Proc. Am. Acad. Arts & Sci.*, 36 (1901), 255-83.
California—Bardsdale	0.892 at 20°	84.17	12.2	..	1.5	1.25	
California — Adams' Canyon	0.921 at 30°	.....	.....	..	0.9	1.46	
California—Torrey	0.8837 at 20°	86.0	12.5	..	0.5	1.15	
California—Sespe	0.8782 at 20°	.....	.....	..	0.45	1.25	
Texas-Beaumont	0.912	85.0	12.3	..	1.75	....	Richardson, C., and Wallace, E. C., *J. Soc. Chem. Ind.*, 20 (1901), 691.

TABLE XVII—(*Continued*)

MID-CONTINENT PETROLEUMS

Source of the Oil	Specific Gravity	Per Cent C	H	O	S	N	Observer and Reference
Kansas (Humbolt)	0.912	85.6	12.4	..	0.37	....	Bartow & McCallum, *Trans. Kan. Acad. Sci.*, 19 (1903), 58.
Kansas (Towanda)	.....	84.15	13.0	..	1.9	0.45	R. Cross, *Bull. No. 16*, Kansas City Testing Lab., p. 184.
Oklahoma (Healdton) ..	.....	85.0	12.9	..	0.76	....	R. Cross, *Bull. No. 16*, Kansas City Testing Lab., p. 184.
Oklahoma	.....	85.7	13.1	..	0.40	0.30	R. Cross, *Bull. No. 16*, Kansas City Testing Lab., p. 184.

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Chapter III.

General Outline of the Manufacture of Petroleum Products.

Three types of petroleum are distinguished in a broad way. These are designated as oils of "paraffin-base," "asphaltic-base," and "mixed-base." The terminology refers in a qualitative way to the chemical composition of the crude oils. This has been discussed in Chapter II, and is recalled here only to point out that the difference in chemical composition determines the refinery practice used in manufacturing marketable products. Thus in a general way, the refinery technology of the plants in Pennsylvania, West Virginia, Ohio, and New York was designed to handle paraffin-base oils, and that of the Gulf Coast refineries (in part) and of the California refineries to handle asphaltic-base oils. Lines cannot be drawn too definitely, for crude oils vary in composition, not only from district to district and from pool to pool, but often from well to well on a given tract.

The following outline of methods is supplemented in other chapters by further discussion of individual operations. In order to show the relationship between the production of motor fuel and other petroleum products, the outlines given here cover the manufacture of the more important petroleum products.

The growth of the petroleum industry has been phenomenally rapid, and there is little to indicate that future development will not be as spectacular as that of the past. Oil skimmed from the surface of springs and ponds was valued by the Indians for its supposed curative properties. The white man learned its value from his red brother and proceeded at once to commercialize his knowledge by selling the oil as a cure-all. One can truly say that the oil industry had its inception in the demand created by the mystery of the patent medicine bottle.

On August 28, 1859, the famous Drake well, the first in the world, came into production on Oil Creek, near Titusville, Pennsylvania. Then came the stimulus of Professor Silliman's previously written (April 16, 1855) classic report on the possibilities of utilizing "rock oils"; and, following that, commercial development. Gasoline or naphtha was a waste product and a nuisance in those early days, as was also the heavy portion of the oil called "tar." Commercial interest centered in burning oil or kerosene. But the invention and use of the automobile changed the whole situation in a most fundamental way.

Gasoline is now the most valuable product of the industry. The stable demand for this product sustains the industry through periods of business stress. Lubricating oils, kerosene, and fuel oils, important as they are, have been forced to acknowledge the commercial supremacy of gasoline.

The Report of Professor Silliman on "Rock Oil."

The classic document of the oil industry is the report of Professor B. Silliman,[1] written for Messrs. Eveleth, Bissell, and Reed, covering his opinion on the economic value of the "Rock Oil" of Venango County, Pennsylvania. This is dated April 16, 1855. At the time of Professor Silliman's researches, there was no guide to knowledge in this field. "Rock Oil" oozed from pits dug in the soil, and floated on the waters of Oil Creek as a heavy dark green fluorescent oil. But Professor Silliman was possessed of extraordinary investigational ability and judgment. His report calls attention to nearly all the possibilities in the utilization of petroleum that have since been developed.

The existence of "tar springs" in the Western United States, and of oily exudations in Baku and in Persia, was mentioned, thus forecasting the production of oil that was to come. Rock oil was shown to be a complex mixture of hydrocarbons, and hence different from the vegetable and animal oils. Chlorination yielded products possessed of odors and tastes resembling chloroform. Oil gas was made by passing the oil through a wrought iron retort filled with carbon and heated to redness. Thermal decomposition in the liquid state was observed and commented on as being a probable method for the production of valuable products, thus forecasting liquid-phase cracking. One of the heavy fractions of the oil that had been heated in a still in such a manner as to cause some thermal decomposition was observed to contain paraffin crystals that could be separated as a white body resembling spermaceti, and from which excellent candles could be made. By slow distillation the burning oils and lubricating oils were produced. Photometric experiments were made using a specially designed instrument. And, as if for good measure, the report closes in these words, "There are suggestions of a practical nature as to the economy of your manufacture when you are ready to begin operations, which I shall be happy to make, should the Company require it—meanwhile, I remain, gentlemen, your obedient servant, B. Silliman, Jr."

The chemical engineer and refinery engineer of today needs only to read this report to introduce himself to all his shortcomings, and to obtain that humility of spirit that for each of us is necessary lest we become complacent and satisfied. Apparently, the only modern product of great importance that did not receive its due share of recognition in Professor Silliman's report was gasoline. But, as the oil examined had probably been exposed in such a manner as to have lost

[1] *The Am. Chem.*, 2 (1871-72), 18-23.

the most volatil portion, his failure to predict the advent of Selden and Ford may perhaps be charitably overlooked.

The foregoing all too brief account of Professor Silliman's work is the most fitting introduction to a review of the technology of the industry.

The Manufacture of Products from Paraffin-Base Petroleum.

The refiner of paraffin-base petroleum uses either or both of two general procedures. When he desires to produce the maximum quantity of high grade lubricants the crude oil is distilled with "fire and steam," that is, part of the heat required is furnished by direct contact of hot flue gases with the bottom of the still, and part by steam that is supplied by perforated pipes placed close to the bottom of the still. The use of steam allows the distillation to proceed at a much lower temperature than in distillation without steam. During the early part of the distillation the difference in the temperature of the oil in the still in these two procedures is about 100° F. During the distillation of the heavy naphtha and kerosene, the temperature difference is 125 to 150° F., and in the latter part of the distillation 175 to 225° F. The result is that little thermal decomposition of the high molecular weight hydrocarbons occurs, and a large yield of lubricating stocks is obtained.

The second procedure is known as the "cracking distillation," and, as the name implies, conditions are so adjusted that the higher hydrocarbons are thermally decomposed to a moderate extent. The "cracking distillation" should not be confused with the cracking processes that have been developed in the last decade. The "cracking distillation" is used when the object of the refiner is to produce a maximum quantity of gasoline, naphthas, and burning oils rather than neutral oils and cylinder stock.

Each of these processes will now be briefly outlined. No two refineries use exactly the same procedure, for each oil presents its own peculiar problems. This must be kept in mind in reading any discussion of the subject.

The Refining of Paraffin-Base Petroleum by Fire and Steam Distillation.

The oil is charged into horizontal cylindrical stills, of 200-barrel to 1000-barrel capacity, that are provided with perforated steam coils placed near the bottom of the still. The still is filled about three-quarters full, and the fire is started. As soon as the temperature of the oil in the still is well above the boiling point of water, steam is admitted through the perforated coils.

The first product to distill is the benzine or crude naphtha. This may constitute 27-40 per cent of the total volume of the crude oil. The vapor from the still passes through the vapor lines to the condenser coils where it forms a liquid that finally exits from the condenser,

passes through the "look-box" and to the "run-down" or temporary storage tank. The still-man ordinarily controls the distillation procedure by noting the specific gravity of the "stream," that is, of the liquid flowing through the "look-box." He may take the gravity with an hydrometer or with a specific gravity balance. The usual method is to express the readings in terms of the Baumé scale for liquids lighter than water, or, more recently, the A. P. I. scale.[2]

The benzine or crude-naphtha cut is collected as the Baumé gravity of the stream drops to 48 to 50°. When the gravity of the stream is 48 to 50° Bé., depending on the practice in the particular plant, the still-man changes the valves on the look-box manifold so that the distillate will flow to another run-down tank. The kerosene distillate is now collected until the gravity of the stream is 42 to 38° Bé. This cut may constitute 15-20 per cent of the volume of the crude oil.

The next distillate is the gas-oil or fuel-oil, which collects while the gravity of the liquid flowing in the look-box changes from 42-38° Bé. to 36.5° Bé. This distillate may constitute 10 to 15 per cent of the crude oil.

The still-man again changes the valves to collect the "wax-distillate," which includes the oil distilling while the gravity of the stream changes from 36.5° Bé. to 31-33° Bé. The fire-test is also used to determine when the wax-distillate is completely distilled. Depending on the plant practice, a fire-test of 600 to 650° F. for the liquid flowing in the look-box would determine this point. The wax-distillate may comprise 16 to 22 per cent of the crude oil.

A residue now remains in the still. This is known as steam-refined cylinder stock, and comprises 12 to 17 per cent of the crude oil. The cylinder stock is pumped out through a pipe-cooler to a storage tank.

Treatment of the Benzine or Crude Naphtha.

The crude benzine may or may not be refined with sulfuric acid. If it is to be so refined, it is pumped to an agitator where it is treated with 2 to 5 pounds of 66° sulfuric acid per barrel of distillate. The acid is usually added in two or more portions. The first is called the "water-acid," and is intended to dry the oil. The acid and the distillate are brought into contact by means of air agitation. The time of treatment varies from a few minutes to over an hour. It should be as short as possible, and just enough air should be used to roll the oil, in order to avoid excessive loss of the volatil hydrocarbons. After each treatment with acid, the sludge is allowed to settle and is drained from the agitator.

When the acid-treatment is complete, the benzine is washed with water that is sprayed from perforated pipes above the surface of the distillate. Then a 5 to 10° Bé. solution of caustic soda is pumped into the agitator, and the benzine is again agitated with air. Finally the caustic solution is drawn off, and the distillate is again sprayed with

[2] See Chapter XVI.

water. As a result of all this treatment 2 to 4 per cent of the crude benzine will be lost. It is questionable if the betterment of color and odor is of sufficient importance in many cases to warrant the loss.

Following the refining treatment the benzine is distilled from a steam-still fitted with a fractionating tower and open and closed steam-coils, or from a fire-still equipped with open steam-coils and a tower. The temperature of distillation is lowered 100 to 150° F. by the use of open-steam, and the products so produced are "sweeter" and of better odor than those made at the higher temperature attendant on distillation without steam. Compounds formed during the sulfuric acid treatment dissolve in the benzine and decompose readily at the temperatures reached in fire-distillation without steam. The various grades of gasolines and refined-naphthas (70° Bé. to 54° Bé.) are thus produced.

The residual oil in the steam-still, or the "still-bottom" as it is called, is pumped to a storage tank, and when a sufficient amount has accumulated it is re-run in a fire-still. The products are crude benzine, kerosene distillate, and a fuel-oil still-bottom. These are added to the respective fractions distilled from the crude oil.

Treatment of the Kerosene Distillate.

The kerosene distillate is reduced with steam until the oil in the still is of the proper flash and fire point. It is then pumped to a storage tank where it cools. The cold distillate is then refined with sulfuric acid in much the same way that the crude benzine was handled. The main differences are that 4 to 6 pounds of acid are used per barrel of kerosene distillate, the time of agitation with the acid is one and one-half to two hours, and two to three times as much water is used in washing the oil. If the color is not water-white the oil may be agitated with pulverized fuller's earth, or filtered through fuller's earth.

Several grades of burning oil may be produced depending on how the cuts were made in the distillation of the crude oil. If a cut was made when the gravity of the stream was 41 to 42° Bé., the refined product will be 150° F. fire test W. W. kerosene. The cut from 41° Bé. to 38° Bé. would then be worked up as a product called mineral colza, mineral seal oil, or "300" oil.

The Gas or Fuel Oil.

This distillate is steam reduced to remove any kerosene distillate. The gas- or fuel-oil residue is sold to the manufacturers of carbureted water-gas, or as a light fuel-oil. Since the development of the absorption process for the manufacture of natural-gas gasoline, gas-oil has found a market as scrubber oil. The larger companies do not sell their gas-oil, but crack it to produce gasoline and other distillates.

Treatment of the Wax-Distillate.

The wax-distillate contains some crystalline paraffin wax, but most of the wax is in colloidal form. The first operation consists in re-running the distillate in fire-stills. A small amount of open-steam is used. This procedure serves to separate the lower boiling products and, in plant lingo, to "crack the amorphous wax." The benzine, kerosene, and fuel oil separated are added to the respective cuts from the crude oil. The still-residue is added to the wax-distillate from the crude.

The "cracked" wax-distillate is pumped to chilling machines and cooled to 15 to 30° F. by means of circulating calcium chloride brine. A soft mush, composed of oil and wax crystals, is formed. The wax comprises 10 per cent of the whole.

The oil-wax mush is pumped to filter-presses where the oil is squeezed through canvas filtering media. The wax is held in the frames of the press. A pressure of 300 to 400 pounds is used. The oil flowing from the press is known as pressed distillate, and 80 per cent of the wax-distillate is obtained in this form. The wax from the presses is called slack-wax. It is about one-half wax and one-half oil.

The slack-wax is moved to melting-tanks by means of a conveyor. The melted wax is then pumped to the sweat-pans. These are steel pans, perhaps 8′-0″ x 20′-0″ x 1′-2″ deep, placed one above another in a tight brick building or "oven." The pans are fitted with a taut galvanized iron or brass screen, placed 6″ to 8″ below the top, and with pipe coils above the screen. Cold or hot water can be circulated through these coils. The building is provided with steam-heating coils, and the temperature is thermostatically controlled.

The pans are filled with cold water to a height of ¼″ above the screens, and then the melted wax is pumped in. Cold water is circulated through the coils to solidify the wax. As soon as the wax is solid the water is drawn off, and the cake of wax and oil settles onto the screen. The temperature inside the building is now carefully raised. The oil slowly separates or "sweats" from the wax and drips into the pan. Within twenty-four hours the oil should be separated.

The oil that sweats from the wax during the first part of the operation is called footes oil. It is added to the wax-distillate from the crude oil. During the latter part of the sweating operation, oil and wax, or intermediate-wax, drips from the wax on the screen. This is added to the slack-wax.

At the end of the sweating operation the wax cake is melted by raising the temperature above 125° F., and by circulating hot water through the coils in the pan. The wax is of slightly yellowish color, and is filtered through fuller's earth or bone-char. It is then molded into cakes and is ready for the market.

The pressed distillate is reduced with steam, in a fire-and-steam still, to remove the lower boiling oils. In this way cuts of kerosene distillate and gas-oil are collected and added to these distillates from the crude oil. Similarly a lubricating oil fraction of low viscosity is

collected. This is the non-viscous neutral-oil stock. The residue in the still is known as viscous neutral-oil stock. The properties of this stock may be varied to suit sales requirements. To improve the color the viscous-neutral stock is filtered through fuller's earth. The product may be of 30 to 34° Bé., of 150 to 400 second Saybolt viscosity at 100° F., 20 to 35° F. cold test, and 375 to 425° F. flash test.

The non-viscous neutral stock is reduced with steam until the residual oil in the still possesses the desired properties. These oils are also filtered through fuller's earth to produce the non-viscous neutral oils. These may vary in property from 50 to 150 second Saybolt viscosity at 100° F., from 10 to 30° F. cold test, and from 300 to 375° F. flash test.

Treatment of the Cylinder Stock.

The oil remaining in the still at the conclusion of the steam and fire distillation of the crude oil is in part marketed directly as "steam-refined cylinder stock." Some of it may be filtered through fuller's earth to improve the color. The product is then known as filtered cylinder-oil. If "bright-stock" is to be made, the still-residue is diluted with naphtha until the gravity of the mixture is about 42° Bé. The mixture is then pumped to the chilling pans (steel tanks 6 feet deep, and cooled by circulation of the brine from the wax-house) and allowed to stand. The amorphous wax separates. The oil is then re-run to remove the naphtha. The cold test of the product so obtained is lowered 60 to 70° F. below that of the steam-refined stock.

The amorphous or colloidal wax that separates is marketed as a lubricant for stuffing-boxes or the like, or is diluted with naphtha, filtered one or more times through fuller's earth, steam-reduced to remove the naphtha, and sold as petrolatum.

The following table shows an average result in refining a paraffin-base petroleum when steam is used in the initial distillation.

Gasoline and Naphtha	30.0%
Burning Oils	17.5%
Fuel and Gas Oils	22.5%
Light Lubricating Oils	3.5%
Medium Lubricating Oils	4.5%
Paraffin Wax	1.3%
Petrolatum	0.8%
Cylinder Oils	15.0%
Loss	4.9%
	100.0%

The flow-sheet shown in Figure 8 depicts the operations outlined above.

The Cracking Distillation of Paraffin-Base Petroleum.

The products most in demand in the early days of the oil industry were the burning oils or kerosenes. Gasoline was regarded as a waste

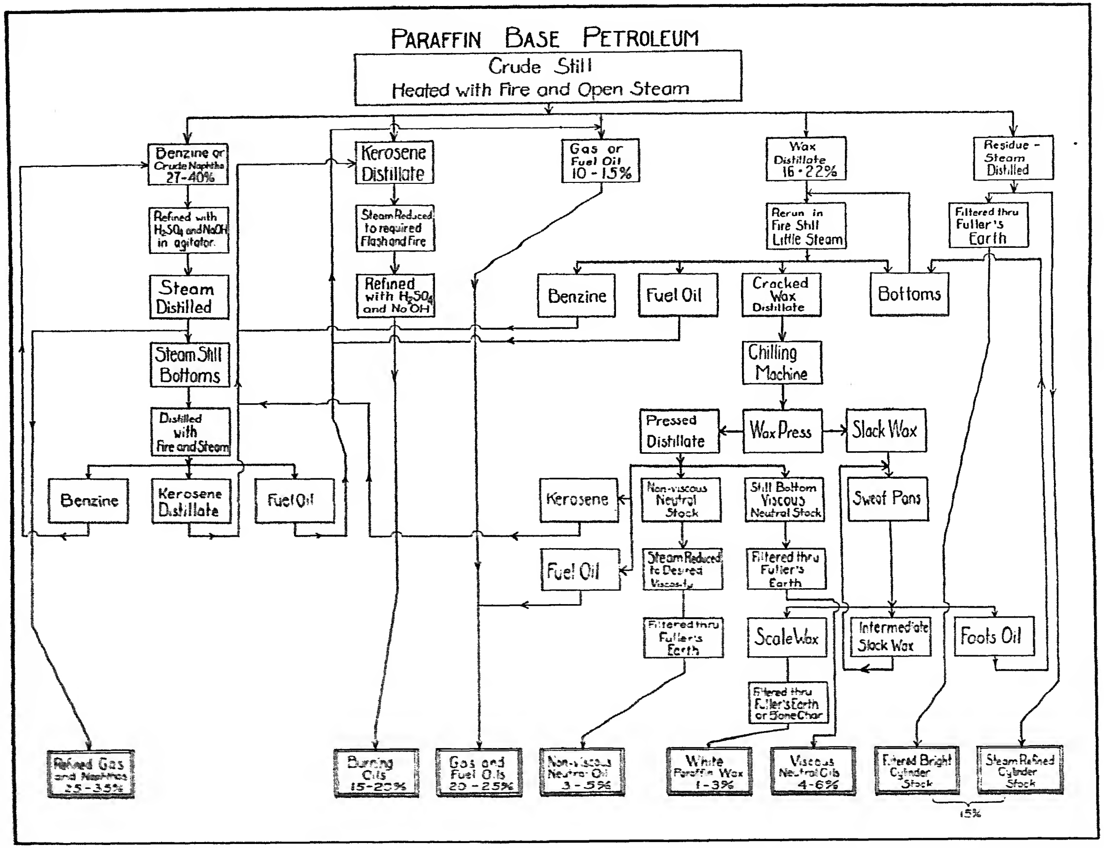

FIG. 8.—Flow-Sheet of Treatment of Paraffin-Base Petroleum by Distillation with Fire and Steam.

product and a nuisance. The aim of the refiner was to include as much of the oil as possible in the kerosene distillates. Municipal regulations and laws regarding the flash point of illuminating oils bear witness to the necessity of curbing the enthusiasm of the refiner in this direction. The development of the automotive industry has changed this situation entirely, but the demand for kerosene in earlier days left its stamp on refinery processes in the shape of the so-called "cracking-distillation."

The "cracking-distillation" differs from the distillation with fire-and-steam in that when the oil in the still reaches a temperature of about 650° F., the rate of distillation is decreased, and a slow heating continued until the temperature of oil in the still has risen 50 to 70° F. Mild thermal decomposition occurs, with production of small amounts of gasoline and larger quantities of kerosene distillate. This process was formerly widely used, but the industrial growth of this and other countries as well as the widespread use of the automobile has created a demand for high grade lubricants. The trade has always regarded the lubricating oils made from paraffin-base crudes very highly, so the tendency has been to use these oils in large measure for the manufacture of lubricants. The cracking-distillation of paraffin-base oils is of less importance today than formerly.

As the years passed, petroleum was discovered in Indiana and Illinois, and in the districts of the Mid-Continent. These oils were thought to be not so well suited for the manufacture of lubricants. Hence the growing demand for gasoline after 1900 resulted in the application of the cracking-distillation to the mixed-base petroleums.

The Cracking-Distillation of Mixed-Base Petroleum.

Any description of a process for refining mixed-base petroleum must be interpreted with much latitude. The crude oils differ widely in their properties, and every refiner has evolved methods and apparatus that he believes to be the best suited to his requirements.

In my opinion there is little excuse for using the "cracking-distillation" today, as better results can be obtained by a combination of processes for the continuous removal of the lighter distillates, for cracking the middle distillates under carefully controlled conditions, and for working up the 35 to 45 per cent of "tar" or residuum to produce either gasoline, distillates and fuel oil, or lubricating oils and fuel oil, as may be required. However, a description of the "cracking-distillation" follows.

The crude oil is distilled from a fire-still that is fitted with a "tower" or fractionating-condenser. The crude benzine is first removed. When the gravity of the stream reaches 46.5 to 47° Bé. the distillate is directed to the run-down tank for kerosene distillate. The crude benzine may be treated with acid and caustic soda and then steam-distilled, may be steam-distilled only, or, if the fractionating tower is effective, and the odor of the distillate not offensive, it may

be sold without any treatment. The procedures are practically identical with those already given for handling the benzine from paraffin-base oil. The gasolines produced vary in gravity from 54 to 74° Bé., have initial boiling points of 100 to 140° F., and end-points of 350 to 460° F. The color and odor depend on the chemical treatment.

The second fraction, or kerosene distillate, is composed of the oil that distills as the gravity of the stream changes from 47 to 37° Bé. The temperature of the oil in the still (no steam used) will now be about 625° F. The kerosene distillate is steam reduced to the proper flash point if necessary, and then treated with sulfuric acid and caustic soda as already described for paraffin-base kerosene.

The fire under the still is now slackened so that the distillation proceeds slowly. The slower the distillation the more extensive the cracking. The "cracked-distillate" is collected while the temperature of the oil in the still rises 50 to 75° F., and its volume may be 20 per cent of that of the crude oil. A "tar" or "residuum," 40 to 45 per cent of the volume of the original crude, now remains in the still.

The cracked-distillate is distilled with fire and steam yielding 4 to 5 per cent of crude benzine. This benzine is treated with acid and soda and steam-distilled. The next fraction is a crude kerosene distillate that must be treated with acid and caustic, and distilled with steam to produce standard-white distillate. The residue in the still is gas-oil or fuel-oil, and more of this is obtained from the steam-still.

The fire is increased under the crude-still, and the "tar" distilled more rapidly. Some cracking occurs. The products of the operation are 14 to 18 per cent of cracked-distillate. 20 to 25 per cent of "paraffin-distillate," 1 per cent of wax-tailings, and 4 to 5 per cent of coke. The cracked-distillate is added to the similar fraction obtained from the crude. The paraffin-distillate is treated further. The wax-tailings are composed of high molecular weight hydrocarbons, some of them, as for example chrysene and anthracene, of the aromatic series. It is used in water-proofing compounds, in axle-greases and other very cheap greases, but is more often added to fuel or road oils. The wax-tailing is not allowed to enter the condenser coils, but is passed directly to a small tank or wax-pot where it condenses.

The paraffin-distillate is the source of the lubricating oils. It is handled in much the same way as the lubricating distillate from paraffin-base crude. The main difference lies in the fact that the paraffin-distillate must be refined with sulfuric acid and caustic soda to remove easily oxidizable hydrocarbon substances. The distillate is chilled, filter-pressed to remove the slack-wax, and the pressed paraffin-distillate distilled with steam. The slack-wax is refined in the ordinary way to make white paraffin wax. The steam-distillation of the pressed paraffin-distillate yields gas and fuel oil, and paraffin oil lubricating stock. The nature of the lubricating oil desired determines how far the stock is reduced with steam. The oil in the steam-

still at the end of the reduction may be ⅙ to ½ of that charged into the still.

The "paraffin" lubricating stocks are refined in an agitator with 10 to 50 pounds of sulfuric acid per barrel of oil. The loss in volume is as much as 10 to 30 per cent. The products are known as "paraffin" lubricating oils. They should not be confused with the "paraffin-base" lubricants made from paraffin-base crudes.

Table XVIII presents a comparison of the results of the "cracking-" distillation and straight-distillation when applied to mixed-base petroleums.

TABLE XVIII

COMPARISON OF THE RESULTS OBTAINED WHEN A MIXED-BASE PETROLEUM IS TREATED BY THE "CRACKING-DISTILLATION" AND BY STRAIGHT-DISTILLATION

	"Cracking-Distillation" per cent	Straight-Distillation per cent
Gasoline	25-35	20-30
Burning oils	15-25	8-12
Gas and fuel oils	30-40	40-50
Lubricating oils	2-5	2-6
Wax tailings	1	.....
Coke	4-5	.....
Loss	4-6	4-5
Miscellaneous	.....	5-10

In Figure 9 a flow sheet is presented that shows the sequence of the operations just described. (See page 67.)

The Refining of Mixed-Base Petroleums by Other Methods.

The refining of mixed-base petroleums is often carried out by distilling the oil with fire-and-steam. The result is similar to that already described for a paraffin-base oil except that the 15 to 18 per cent residuum in the still at the end of the operation contains the asphaltic hydrocarbons and is not suitable for use as a steam-refined cylinder stock. The residuum may be blended with lighter distillates and sold as fuel oil or road oil, or it may be blown with steam and sold as asphalt.

Many small refineries in the Mid-Continent fields are operated as "skimming" plants, that is, the lighter distillates are removed, and these with the residuum or fuel oil are sold in bulk to the larger companies that make and market a complete line of products. The skimming plants are usually located near the source of their crude oil supply.

The writer is of the opinion that the logical plant for the refiner of Mid-Continent oils, as well as asphalt-base oils, will include three divisions. One of these will fractionate the oil without attempting to change the nature of the hydrocarbons, and produce distillates, lubricating oils and residuum. The processes of fractionation, steam-distilla-

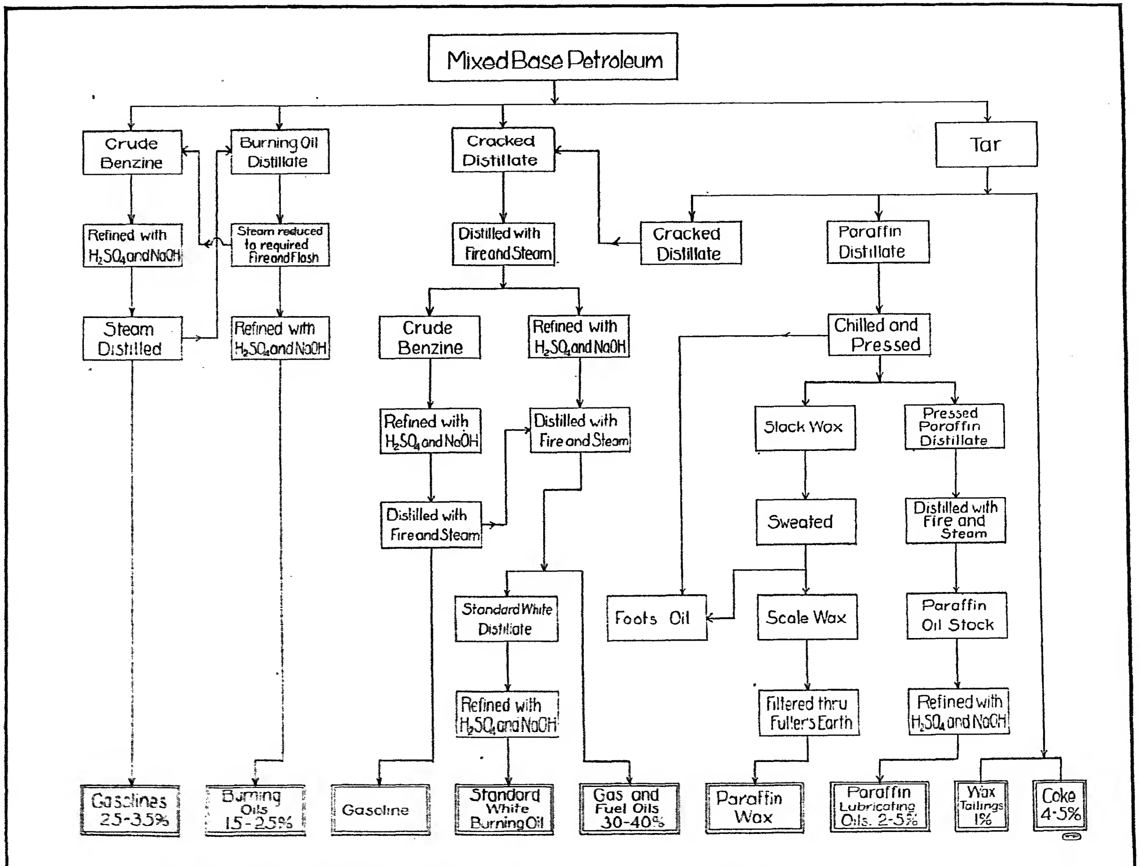

FIG. 9.—Flow-Sheet of the "Cracking-Distillation" of a Mixed-Base Paraffin.

tion, and refining will be of the continuous type wherever feasible. A second division will comprise a cracking plant that will handle the heavy fuel oils, "tars," or residuums, producing therefrom gasoline, distillates, and fuel oils composed of fluxed heavy-residues. The third division will produce gasoline from the middle distillates obtained from the crude-oil and from the heavy-oil cracking-plant. A plant organized in this way would produce the maximum quantity of gasoline to the most salable product, along with burning oils and lubricating oils as required, and blended fuel-oils. It would be flexible and highly profitable. Furthermore it is possible of attainment, for successful methods for producing gasoline from middle distillates and from the heavy tars and residuums are now available.

The Methods of Refining Asphaltic-Base Petroleums.

The asphaltic oils of California, the Gulf Coast, and Mexico were at one time regarded as suitable only for the production of distillates and fuel oil. The methods now in use in refining these oils were developed in California in the main, and have been adapted to the Mexican oils.

The oils produced in the earlier days of the industry in California were heavy and asphaltic. The main object of refining them was to remove a few per cent of the lighter distillates to render the residuum suitable for use as fuel oil. Railroads and industrial establishments were forced to use oil as fuel for coal was not to be had. The "topping-plant," as it is called in California, was the logical development from this situation.

As the years have passed, and newer producing fields developed, lighter oils have been found, so that average California oil now contains 13 to 14 per cent of gasoline and 12 to 15 per cent of distillates.

The larger part of the oil is run through topping-plants. The usual type includes a furnace with pipe-coil heater, and a steel evaporator or closed tank into which the hot oil is discharged and where the vapors are "flashed" from the less volatil portion. The vapors are passed through a series of fractionating condensers. The condensate from each of these is run through continuous steam-stills. The products are gasoline stock (known as "tops"), "slop" or kerosene distillate, stove, furnace, and orchard oils, and residuum.

The yield of these several products varies with the nature of the crude and with the demand. The 26 to 34° Bé. distillates are frequently not removed at all. Table XIX shows the yields in a general way.

The larger refiners in California manufacture lubricants. Statistics for 1921 show that 2.1 per cent of the petroleum refined in California appeared on the market as lubricating oil. Paraffin wax is also made in a limited way. The quantity marketed in 1921 was 1,167,560 pounds. Several refineries in California use cracking processes, particularly to convert a part of the 38° Bé. distillate into gasoline and other naphthas. The limited local market for kerosene, the diffi-

TABLE XIX

PRODUCTS FROM CALIFORNIA PETROLEUMS

Product	Limits per cent	Average Yield if All Products are Made per cent
Gasoline Stock or "Tops." 52-54° Bé.	8–16	13.5
Kerosene Stock or "Slop." 37–39° Bé.	3–7	5.0
Stove Distillate. 30–40° Bé. Orchard Oil and Furnace Distillates	5–15	10.0
Residuum or Fuel Oil. 17–20° Bé....	65–80	71.5

culties in refining to remove aromatic hydrocarbons, and the fact that the Asiatic export market is largely supplied by one company, has made the disposal of the kerosene stock a real problem for most refiners.

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Chapter IV.

Fractional Distillation.

Fractional distillation is the basis of many of the important procedures used in the manufacture of petroleum products. Also the results of plant operation are checked against laboratory data based on fractional distillation. Evaluation of crude oils and identification and examination of products depend upon distillation. Hence a discussion of basic principles, and a critical review of plant and laboratory methods is essential to any treatment of the general subject of motor fuels. The present chapter is confined mainly to the theory of distillation. Plant methods are discussed in Chapters VI and VII, and laboratory procedure in Chapter XV.

The theoretical discussion that follows is mainly confined to systems of two components. Present knowledge of more complicated systems is very limited. But this is in fact less of a handicap than it may at first appear, for, although petroleum is a complex mixture of hydrocarbons, the refiner is not interested in separating the component substances. Rather, he is concerned with the production of several mixtures—gasoline, kerosene, gas-oil and other middle distillates, lubricating oils, fuel oils, and residuum. The more volatil of these products are obtained by a process of vaporization and condensation. The less volatil remain as residues in the still. In a qualitative way the separation of petroleum, by batch distillation, into gasoline and a residue in the still, is analogous to the separation of the more volatil substance A from a mixture of A and B. A discussion, therefore, of the distillation of simple systems will be helpful in understanding the principles that are, or should be, the basis of refinery operations.

The Kinetic Conception of Vapor-Pressure.

Liquid water is composed of small entities of definite composition called molecules. These are in constant motion. Some move slowly and others rapidly, and at every temperature there are those that are possessed of sufficient kinetic energy to break through the surface film of the water to enter the space above. These molecules in the vapor space are also in constant motion. The force of their impacts on any surface that may be interposed is the pressure known as the "vapor-pressure" of the substance at any particular temperature. The motion of the molecules in both liquid and vapor is disordered, that is, they move in every direction. As a consequence of this, not only do molecules leave the liquid to enter the vapor, but they also enter the

liquid from the vapor. The number entering and leaving the liquid or the vapor will always be equal if a small time interval is allowed for the system to reach the condition that is commonly referred to as "equilibrium."

If the temperature of the water is raised, the kinetic energy of the molecules is increased. Their velocity is increased. More molecules leave the liquid to enter the vapor, and hence each unit volume of the vapor contains more molecules. The vapor-pressure is increased, both because in unit volume there are more molecules than before and because the molecules move more rapidly. After the passage of a reasonable interval of time, equilibrium will be established at the higher temperature.

The effect of a given temperature increase is not the same for hexane as for water. In general it may be said that the rate of increase of vapor-pressure with temperature is different for each and every substance. If the values of the vapor pressures are plotted against the corresponding temperatures, a curve will be obtained known as the vapor-pressure curve of the substance.

The temperature at which the vapor-pressure of the substance equals the external pressure, when vapor and liquid are in equilibrium, is known as the boiling-point of the substance. It is the temperature at which the pressure of the molecules of the vaporized substance is just sufficient to push the air or other gas away. If heat is continuously supplied to the system at this temperature the liquid is continuously "vaporized." The "normal" boiling-point of a substance is the temperature at which the vapor-pressure is 760 mm. of mercury.

Vapor-Pressure of a System Composed of Two Immiscible Liquid Substances.

Assume that liquid substances A and B are not soluble in each other. The vapor-pressure exerted by a mixture of these liquids is the sum of the vapor-pressures of the two liquids, or

$$P_M = P_A + P_B$$

in which P_M is the vapor-pressure of the mixture. When P_M equals the total pressure on the system the mixture of liquids will boil. Obviously the temperature at which the mixture will boil is less than the boiling point of either of the liquids A or B. This is the theoretical basis of the process known as steam distillation, which will be discussed in later sections.

The Vapor-Pressure of Solutions.

A solution may be defined as a physically homogeneous mixture of two or more substances.[1] Thus solutions may be gaseous, liquid,

[1] The word "substance" is frequently used in a loose sense, but should be reserved to designate a species of matter, that is, matter of which all specimens are possessed of the same specific physical properties.

or solid. In the study of fractional distillation we are interested in liquid mixtures of substances, or liquid solutions, and in the composition of the vapor in equilibrium with them.

Solutions are designated as dilute or concentrated. While there is no definite boundary between the two classes, solutions may arbitrarily be called dilute when they contain less than 2 mols of one substance in every 100 total mols.

Raoult's Law of Vapor-Pressure Lowering.

The addition of a liquid substance A to a liquid substance B lowers the vapor-pressure of B. This is as would be expected if the solution so formed is considered from the standpoint of the kinetic molecular hypothesis. The lowering of the vapor-pressure of B, in dilute solutions, is proportional to the mol-fraction of A, or

$$P = P_0 X_0$$

in which P_0 is the vapor-pressure of pure B, X_0 the mol-fraction[2] of B in the solution, and P the vapor-pressure of B from the solution. This expression is known as Raoult's Law.

Raoult's Law presupposes[3] that the vapor of the substance behaves in accordance with the perfect gas laws. It is applicable only to dilute solutions.

Henry's Law, and the Vapor-Pressure of the Solute.

We have just seen that the vapor-pressure of the solvent in a dilute solution can be calculated by use of Raoult's Law. By means of a similar simple relationship the vapor-pressure of the solute, or substance A, can be calculated.

$$P = KX$$

[2] The mol-fraction $X_0 = \frac{N_0}{N + N_0}$, in which N = mols of A, and N_0 mols of B, in any mixture of A and B.

[3] Raoult's Law is an integrated form of the general vapor-pressure law that is written:

$$\frac{dp_B}{dx_B} = K_B$$

By integration:

$$P_B = K_B X_B + I$$

When $X_B = 0$, $P_B = 0$ also, and the integration constant $I = 0$. When $X_B = 1.0$, that is, when the "solution" is pure B, $K_B = P_B$ or, stated in words, the proportionality constant K_B is the vapor-pressure of pure B. Hence the general expression is written $P = P_0 X_0$ in which the symbols have the significance already given in the context.

It is apparent that if the equation is to be applied as a means of calculating the tendency of molecules of B to escape from the solution, the vapor must behave as a perfect gas. If the vapor does not so behave, corrections must be applied that will compensate for the deviations of the gaseous phase. If the modified perfect-gas law for moderate pressures is written $PV = NRT(1 + \alpha p)$ the corrected Raoult Law is

$$P = P_0 X_0 e^{\alpha(P_0 - P)} = P_0 X_0 [1 + \alpha(P_0 - P) + \tfrac{1}{2}\alpha^2 (P_0 - P)^2 + \text{------}]$$

This relationship is known as Henry's Law, and may be stated: The partial vapor-pressure of a substance present in small amount in a solution is proportional to its mol-fraction. The law holds rigorously only for dilute solutions.

Henry's Law may be regarded as expressing the distribution of the molecular species A between the vapor and liquid phase. When applied to substances that are gases at ordinary temperature it is often stated, "The solubility (concentration of the saturated solution) of any gas is proportional to the pressure at which the gas is supplied."

The Vapor-Pressure of Concentrated Solutions.

Concentrated solutions may be classified into two groups:

Type I. Concentrated perfect solutions are those solutions whose formation from their components is not attended by evolution or absorption of heat, or by volume change. The properties of these solutions approximate those that are calculated by taking into account additively the properties of the components and the composition of the solution. The laws of dilute solutions apply approximately to this type concentrated solution, the more closely the more nearly the solution conforms to Type I.

Type II. Solutions whose formation is attended by energy change, as shown by evolution or absorption of heat and by volume changes. No laws are now known that are generally applicable to solutions of this type.

While I have thus designated two general classes of concentrated solutions, there is in reality no sharp dividing line. Fortunately most of the solutions that are of interest to the petroleum refiner approximate Type I, and will be referred to as concentrated perfect solutions even though they do not exactly fulfill the requirements as defined above. The vapor-pressure of each component of a concentrated perfect solution can be approximately calculated by Raoult's Law, that is, the partial vapor-pressure of any component is nearly equal to the product of the vapor-pressure and mol-fraction of the component, i.e.,

$$P_A = P_{OA}X_A, \ P_B = P_{OB}X_B, \text{ etc.}$$

Raoult's Law must be regarded as a limiting law from which there will be divergence in some degree.

A common method for experimentally determining the partial vapor-pressure of such solutions, at any given temperature, is to heat a mixture of known composition, and to adjust the pressure until the solution boils at the chosen temperature. A small quantity of distillate from a large volume of solution is then analyzed. From data obtained in this manner an isothermal total-pressure curve can be drawn for the binary mixture (solution of two components). Compositions [4] of the

[4] Composition is expressed in terms of weight-per cent or mol-per cent of the more volatil component B.

liquid mixture are plotted on the horizontal axis and vapor-pressures on the vertical axis. Curve I of Figure 10 is a typical isothermal vapor-pressure curve for a concentrated perfect solution composed of substances A and B. If the solution were perfect, the curve would be a straight line.

Curves II and III of Figure 10 are typical isothermal vapor-pressure curves of solutions of two components that do not conform to the laws of concentrated perfect solutions within any reasonable degree of approximation. To understand how solutions can show vapor-pressures higher or lower than that of either component, and the

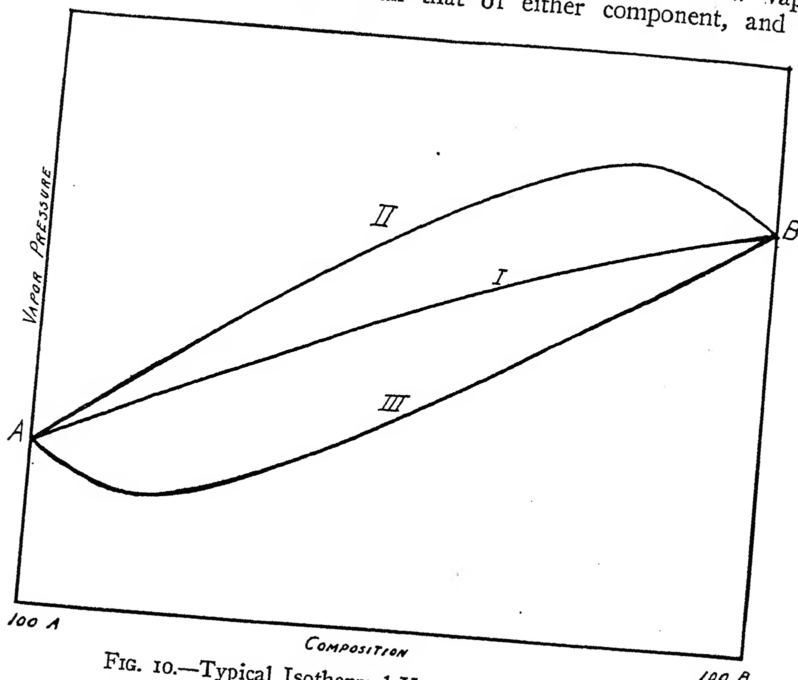


Fig. 10.—Typical Isothermal Vapor-Pressure Curves.

vapor-pressure curve a maximum or minimum, it is necessary to consider the various possible effects of the addition of component B to A. These possibilities are five in number:

1. The B molecules may exert the same attraction or forces on the A molecules as the latter exert on each other. The addition of B to A therefore produces no disturbance of the molecular force relationships, and the partial vapor-pressure of each component is equal to P_0X, that is, the product of the vapor-pressure of the substance and the mol-fraction. The vapor-pressure curve will be a straight line in this case.

2. The molecules of B may attract A molecules more strongly

than the A molecules attract each other. In this event, the number of A molecules entering the vapor from the solution will be lessened. The vapor-pressure of A from the solution will be less than proportionate to the mol-fraction of A. Admixture of A and B will be attended by diminution in volume, that is, the volume of the solutions will be less than the sum of the volumes of the two components mixed. Heat will be evolved. The vapor-pressure curve will be convex downward, and will lie below the straight line connecting points A and B in Figure 10.

3. The molecules of B may attract A molecules less strongly than the A molecules attract each other. The number of A molecules entering the vapor will be greater than proportionate to the mol-fraction of A. The mixing of A and B will be accompanied by an increase in volume, and the temperature of the solution will fall. The vapor-pressure curve will lie above a straight line connecting points A and B in Figure 10.

4. The B molecules may combine chemically with the A molecules to form AB, A_2B, AB_2, or other compound. The concentration of A molecules is thus lessened not only by the presence of B molecules, but also as a result of the chemical reaction and of the presence of the molecules of the compound. The result will be a smaller vapor-pressure than would be indicated by Raoult's Law. Decrease in volume and rise in temperature usually are a part of the phenomenon. The vapor-pressure curve will lie below the straight line connecting points A and B in Figure 10.

5. If the molecules of the solvent associate to form A_2, or A_3, or both, the addition of B will result in the partial dissociation of di- or tri-molecular A compounds. Heat will be absorbed as is usual in dissociations, and the temperature will fall when B is added. The concentration of A molecules becomes greater, and hence the vapor-pressure is increased. The vapor-pressure curve will lie above the straight line connecting points A and B in Figure 10.

Obviously two or more of these effects may be combined, so that the resultant or apparent effect may be less or greater than if one phenomenon alone were involved. The vapor-pressure curve may diverge only slightly from a straight line, or it may diverge so markedly as to show a maximum or minimum as illustrated respectively by the type curves II and III of Figure 10. Vapor-pressure curves similar to II are fairly common. Young[5] summarizes the relationships between vapor-pressure and composition of binary mixtures as follows:

"1. When the two components are very closely related chemically, the changes of volume and temperature on mixing the liquids are small.

[5] Young, S., "Fractional Distillation," 1903 Edition, pp. 32-43; 1922 Edition, pp. 27-35.

"2. When the chemical relationships are close, and the critical pressures equal, the vapor-pressure of the mixture may be accurately calculated by the formula:

$$P = \frac{mP_A + (100 - m)P_B}{100}$$

That is, the relationship between vapor-pressure and molecular composition is a straight line.

"3. When the components are very closely related chemically, but the critical pressures are not equal, the percentage difference between the observed and calculated pressures is very small, even when there is molecular association in the liquid state.

"4. When the components are not closely related chemically, even if there is no molecular association the calculated (from the formula under 2) vapor-pressure of the mixture is, as a rule, different in moderate to large degree from the observed vapor-pressure.

"5. When the components are not closely related chemically, and when there is molecular association in the liquid state, the differences between observed and calculated vapor-pressures is usually large."

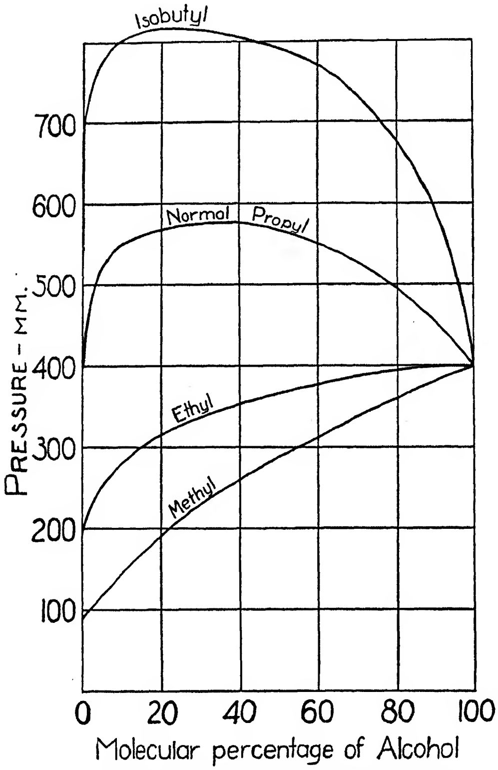


Fig. 11.—Vapor-Pressure Curves of Solutions of Water and Lower Alcohols.

The vapor-pressure curves [6] of mixtures of water with the lower alcohols, shown in Figure 11, is illustrative of possibilities in divergence from a straight-line vapor-pressure curve. The temperatures were such that the vapor-pressure of each pure alcohol was 400 mm. of mercury. Methyl alcohol is most nearly like water, and the vapor-pressure curve of its mixture with water is of Type I (Fig. 10), in which no maximum is shown. The curve for mixtures of ethyl alcohol

[6] Young, "Fractional Distillation," 1922 Edition, p. 36.

and water shows a maximum at about 95 per cent alcohol, and curves for both of the other alcohol-water mixtures show very sharp maxima. A large part of the molecule of isobutyl alcohol resembles the hydrocarbons rather than water. This change in chemical nature accounts for the marked change in the form of the vapor-pressure curve for mixtures of isobutyl alcohol and water as compared to that of mixtures of methyl alcohol and water.

Vapor-Pressure Composition Diagrams.

In Figure 10 vapor-pressure curves of three types were presented. It should be noted that the vapor-pressures were measured at the same temperature, that is, the curves are isothermal total vapor-pressure curves.

Diagrams of this sort are made more instructive by plotting thereon the points representing the composition of the vapor in equilibrium with liquid of various compositions. Such diagrams are necessarily constructed if one is to know the possibilities of isothermal fractional distillation or of constant-temperature condensation when vapor-pressure equals total pressure. While it is true that fractional distillation is ordinarily conducted in such a manner that pressure is constant and temperature changing, constant temperature refluxing or partial condensation, when vapor-pressure equals total-pressure, is not uncommon. The production of a condensate that is richer in the less volatil component and of a vapor richer in the volatil component depends on the fact that the vapor in equilibrium with the solution is richer in the volatil component than is the solution.

Figure 12 shows an isothermal Type I vapor-pressure curve marked "liquid" on the diagram. The curve marked "vapor" shows the composition of the vapor in equilibrium with liquid of any composition. For example, the diagram shows that a liquid of composition C_1 has a vapor-pressure represented by the length of the vertical dotted line drawn from point C_1 to intersect the "liquid" curve. The composition of the vapor may be obtained by projecting horizontally from the "liquid" curve to the "vapor" curve, then vertically to the composition axis. Thus the vapor in equilibrium with a liquid of composition C_1 is of composition C_1'.

If the system is of such a nature that none of the vapor escapes and the external pressure is always equal to the total vapor-pressure, the first vapor formed from a liquid of composition C_1 will have the composition C_1'. But the formation of this vapor results in changing the composition of the liquid so that it is given by some point to the left of C_1. As vaporization continues, the liquid becomes less rich in component B and the vapor-pressure decreases. When the composition of the liquid is C_2 that of the vapor is C_2'. The last minute droplet of liquid will be of composition C_3, and the composition of the vapor $C_3' = C_1$, as is obviously necessary since the entire system, originally liquid of composition C_1, is now in vapor form.

Figure 13 presents a diagram that, in a manner similar to that of Figure 12, shows the total vapor-pressure curve and vapor-composition curve of a Type II solution of two components. The vapor from a binary mixture of this type is not necessarily richer than the liquid in the volatil component B. If the composition is C_1, or any other to the left of the point C_b on the diagram, the vapor will be richer in B than the liquid. But if the composition of the liquid is represented by any point to the right of C_b, the vapor contains less of B than the liquid. Thus the vapor composition C_2' corresponds to liquid composition C_2.

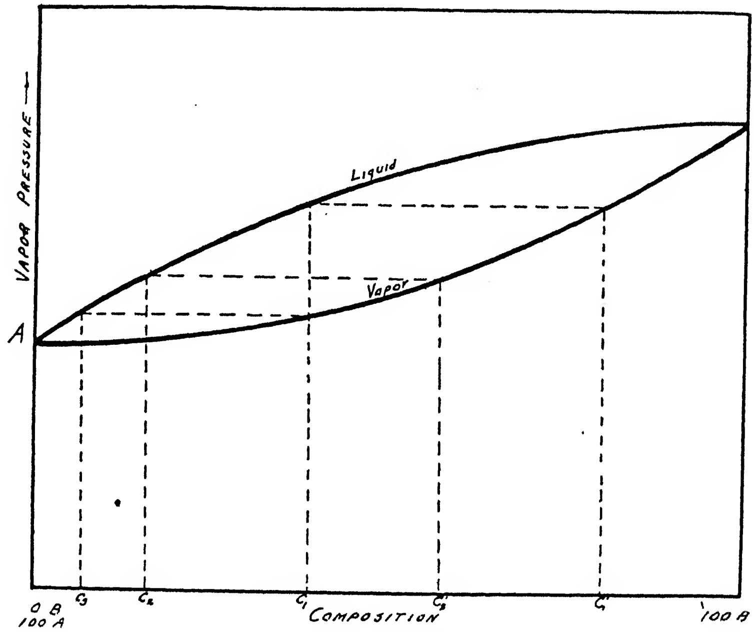


FIG. 12.—Isothermal Vapor-Pressure ~ Composition Diagram of Type I.

If the composition of the liquid is C_b, the vapor is also of composition C_b. The entire quantity of liquid of this composition can be vaporized without change of composition if the external pressure is constant and equal to the total vapor pressure of the liquid.

Solutions showing vapor-pressure curves of Type III are of less importance to the student of motor fuels than those of Types I and II. Examples of Type III mixtures are hydrochloric acid-water, acetone-chloroform and formic acid-pyridine.

'he Detection of Constant-Boiling Mixtures.

Not infrequently, mixtures of constant-boiling point have been istaken for a pure liquid or single substance. However, the com-

position of such mixtures depends on the pressure,[7] and hence they may be detected by distilling at a different total pressure and noting any broadening of the distillation range, and, by analytical means, any change in composition of the fractions. Determinations of specific gravity, index of infraction, and other physical properties are useful in identifying constant-boiling mixtures.

The binary mixture of ethyl alcohol and water is a case in point. The mixture of minimum boiling point contains 4.43 per cent water at 760 mm. pressure. The percentage of water is greater at higher

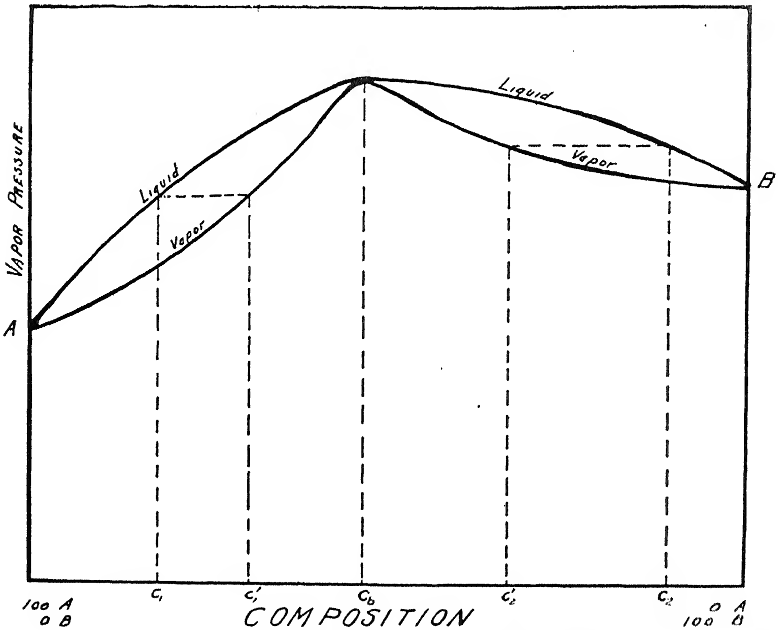


FIG. 13.—Isothermal Vapor-Pressure ~ Composition Diagram of Type II.

pressures. Under diminished pressure the per cent of water in the constant-boiling mixture is less. Below 80 mm. pressure no constant-boiling mixture is formed, and complete separation of the components of the mixture is possible.

When the composition of the constant-boiling mixture is known, the composition of the original binary mixture can then be calculated, since the binary mixture may be separated into excess of one component and constant-boiling mixture.

Sometimes addition of a third component that is not miscible with one of the components can be made the basis of a procedure for separating the substances of which a constant-boiling mixture is composed.

[7] Roscoe, *Liebig's Ann.*, 112 (1859), 327; 116 (1860), 203. Young, *Fract. Dist.*, 1922, pp. 59-61.

Young[8] and Jackson have studied the constant-boiling mixture of n-hexane and benzene. The exact composition is not given, but it lies between the compositions 0 per cent benzene-100 per cent n-hexane and 10 per cent benzene-90 per cent n-hexane.

Lecat[9] has observed the following constant-boiling hydrocarbon mixtures:

Substances		Boiling Points, °C.			Weight Per Cent of A in Mixture (These are none too certain)
A	B	A	B	Mixture of Constant B.P.	
n-Heptane	Methyl-cyclohexane	98.5	101.8	< 98°	> 80
Cyclohexane	Cyclo-hexadiene, 1-3	80.8	80.8	79.2	52
Pinene	Mesitylene	163.8	164	162.7	52
Benzene	Cyclo-hexane	80.2	80.8	77.5	55
Benzene	Cyclo-hexane	80.2	82.8	79.5	85

Lists of mixtures of Types II and III will be found in Young's "Fractional Distillation."[10]

Isobaric or Constant-Pressure Diagrams.

The diagrams that have been presented in the foregoing discussion show the relationship between composition and vapor-pressure when temperature is constant. In practice, however, distillation is seldom conducted isothermally, but nearly always at constant pressure. Atmospheric pressure, of course, fluctuates somewhat, but for the sake of this discussion it may be considered constant.

When it is desired to distill a liquid mixture, the temperature of the liquid is raised until the vapor-pressure of the liquid mixture equals the external pressure. Vapor then forms continuously as long as heat is supplied, and the liquid is said to boil. We are therefore interested in the isobaric diagram, which shows the relationship between liquid-composition and boiling point, and between liquid- and vapor-compositions.

The isobaric diagram can be constructed from data obtained by experimentally determining the composition of the vapor in equilibrium with solutions of various concentrations at the boiling point at the particular pressure. In constructing the diagram temperature is plotted along the vertical axis, and composition, as usual, along the horizontal axis.

The data for constructing the diagram can also be calculated by use of the Clapeyron equation, Raoult's Law, and Dalton's partial-

[8] *J. Chem. Soc.*, 73 (1898), 922-28.

[9] La Tension de Vapeur des mélanges de liquids l'azeotropisme, Brussels, 1918.

[10] 1922 Ed., 49-58.

pressure law. The diagram constructed in this manner approximates to the truth in a degree dependent on the accuracy of these laws in expressing physical relationships for the substances of which the solution is composed. This must always be carefully considered.

Calculation of the Composition of the Vapor- and Liquid-Phases of Binary Systems.

The student of the problems of fractional distillation will frequently desire to calculate the composition of the vapor-phase of a system when that of the liquid is known, or to calculate that of the liquid-phase from knowledge of vapor composition. To make calculations of this nature it is essential to know the vapor-pressure of the pure substances over the temperature range in which the binary system is to be studied.

The relationship known as the Clapeyron equation, which can be derived from the laws of thermodynamics, is an exact differential expression for the rate of change of pressure with absolute temperature.

$$\frac{dp}{dT} = \frac{h}{Tv} \qquad (1)$$

In (1) v is the increase in volume when any definite quantity of the liquid substance at pressure p and absolute temperature T changes to a saturated vapor. The heat required to vaporize the definite amount under the given conditions is h. If the quantity of substance is one mol the equation may be written:

$$\frac{dp}{dT} = \frac{L}{TV} \qquad (2)$$

in which L is the molal heat of vaporization under the given conditions, and V the difference in molal volume of vapor and liquid. The pressure p is at once the vapor-pressure of the substance and the total pressure on the system. If the vapor-pressure and total-pressure are different, as when water and water-vapor are in equilibrium at room temperature and pressure, equation (2) is not rigorous. However, unless one is dealing with a substance near the critical temperature, equation (2), or its integrated forms, are sufficiently accurate.

It is of interest to note again that the Clapeyron equation affords a method for calculating the change of boiling point with pressure, for at the boiling point the vapor-pressure of the substance equals the external pressure.

In order to integrate the foregoing expression, it is necessary to express L and V as functions of T. Over limited temperature range L may be considered a constant, and the expression PV =nRT may be assumed to hold. Also, except near the critical temperature, the volume of the liquid is so small that it may be disregarded, or

$$V = (V_{\text{vapor}} - V_{\text{liquid}})$$

Based on these assumptions the integrated form of equation (2) is

$$\log_e \frac{p_1}{p_2} = \frac{L}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (3)$$

In using this equation L and R must be expressed in the same units. If the molal latent heat is given in small calories the value of the gas-constant R must also be expressed in small calories.[11]

Equation (3) is not exact, as is the differential equation (2). It cannot be more accurate than the assumptions used in integrating equation (2). Latent heats vary with temperature, and the expression $PV = nRT$ holds only for very small changes in conditions when the gas under consideration is an hydrocarbon-vapor.

If the value of L is expressed as a function of T, and if a more exact expression relating the pressure, volume, and temperature of a gas is used, a more exact integrated form of equation (2) will be obtained. But, in most instances, experimental data are lacking that can be used in evaluating the constants in the equation relating latent heat and temperature, as, for example in

$$L = a + bT + cT^2$$

Moreover, it is far easier and more desirable to determine the vapor-pressure curve experimentally than to determine latent heats in order to make possible the calculation of vapor-pressures.

The latent heat of a substance at its normal boiling point can be approximately calculated by use of Trouton's Law:

$$\frac{L}{T_b} = \text{constant} \qquad (4)$$

in which L is the molal latent heat of vaporization, and T_b the absolute temperature at which the substance boils at one atmosphere pressure. The value of the constant is 20-21 for hydrocarbons. Liquids that are associated, such as water, alcohols, and acetic acid, have latent heats widely different from that calculated from Trouton's rule.

A modification of Trouton's rule which gives more nearly correct results is that of Nernst:

$$\frac{L}{T_b} = 9.5 \log_{10} T_b - 0.007\, T_b \qquad (5)$$

but even this does not hold for liquids that, like water, are highly associated.

When the vapor-pressure curve is known for substances A and B, it is possible to calculate the equilibrium composition of the vapor from that of the liquid mixture or solution of A and B, provided these substances form what has been referred to above as concentrated perfect-

[11] $R = 1.9852$ small calories per degree.
$= 0.08207$ liter-atmospheres per degree.
$= 8.3162 \times 10^7$ ergs or 8.3162 joules per degree.

solutions. In this event the law of Raoult holds approximately and affords the basis for calculating the partial vapor-pressure of each component. If such calculations are made for a number of compositions a curve may be plotted, as has already been explained, that will show the composition of the vapor in equilibrium with liquid of any composition.

As has been indicated there are many mixtures of such a nature that the vapor-pressures of the components are not proportional to the mol-fractions. Other formulas have been suggested, among which may be mentioned those of Duhem,[12] Margules,[13] Lehfeldt[14] and Zawidski.[15]

A brief discussion of these formulas is given in Young's "Fractional Distillation" (1903), 104-113; (1922), 88-94.

More recently M. A. Rosanoff and his co-workers have published a series of articles describing the results of their experiments on fractional distillation and in one paper[16] formulate a theory of fractional distillation. The general equation given by Rosanoff for the calculation of vapor composition from the total-pressure curve and the vapor-pressures of the components "1" and "2" is:—

$$\frac{d\pi}{dx} = \left(\frac{P_1 - P_2}{\log P_1 - \log P_2}\right) \log\left[p_1\left(\frac{1-x}{p_2 x}\right)\right] \qquad (6)$$

in which

x = mol-fraction of one of the components in the liquid mixture.

π = the total pressure.

p_1 and p_2 = the partial-pressures of the components in the vapor-phase.

P_1 and P_2 = the vapor-pressures of the pure components of the mixture.

The equation of the isothermal total-pressure curve must be known. This can be derived from experimental data.

As an example of how well the equation reproduces experimental data Table XX showing the observed and calculated total-pressures and vapor-compositions of mixtures of ethyl iodide and ethyl acetate is given. In this case

$$\pi = 280.325 + 250.403x - 285.085x^2 + 210.995x^3 - 103.147x^4$$

Ethyl iodide and ethyl acetate form a mixture that, at 49.99° C., has a maximum vapor-pressure when the content of ethyl iodide is 76.49 per cent. Also association in the liquid state is entirely probable. In

[12] *Ann. de l'Ecole normale Sup.*, 4 (1887), (3), 9; 6 (1889), (3), 153. *Trav. et. Men. de la fac. de Lille*, 1894, III, D.
[13] Sitzungsber. der Wiener Akad., 104 (1895), 1243.
[14] *Phil. Mag.*, 40 (1895), (v), 397; 46 (1898), (v), 42; 47 (1899), (v), 284.
[15] *Zeit. Physik. Chem.*, 35 (1900), 129.
[16] *J. Am. Chem. Soc.*, 36 (1914), 1993-2004.

TABLE XX

ROSANOFF'S DATA ON THE SYSTEM ETHYL IODIDE ~ ETHYL ACETATE

TEMPERATURE 49.99° C.

Molar % C_2H_5 I in the Liquid	π Obs.	π Calc.	Molar % C_2H_5 I in Vapor	
			Obs.	Calc.
5.90	294.3	294.1	9.8	11.1
11.48	304.7	305.3	17.7	19.3
13.76	308.7	309.9	20.9	20.1
19.46	319.5	319.7	27.9	28.6
22.88	325.2	324.9	31.7	32.2
30.57	335.4	335.4	39.0	39.4
37.45	343.4	343.2	45.3	45.4
45.88	350.7	351.0	52.2	52.4
54.86	357.4	357.4	59.7	59.5
63.40	361.7	361.6	66.1	66.1
73.88	363.5	364.1	74.0	74.4
82.53	363.5	363.6	81.5	81.5
90.98	360.7	360.4	89.3	89.4

view of these facts the agreement between observed and calculated values must be considered very good. Several other examples are given by Rosanoff. The difference between observed and calculated total-pressure of benzene and toluene mixtures did not exceed 0.5 mm., and in all except one instance is 0.3 mm. or less.

Derivation of Equations from Experimental Data.

It is frequently either necessary or desirable to know the equation of the curve that passes through a series of points that have been determined by experiment. The most valuable exposition of methods for finding such equations, and for solving numerous related problems, is that of Dr. Theodore R. Running, entitled "Empirical Formulas." [17]

As an example, the equation $y = \frac{x}{0.4 + 0.6x}$, in which x is the composition of the liquid and y the composition of the vapor, both in terms of benzene, and expressed by weight as decimal parts of unity, represents the curve [18] relating vapor and liquid compositions of mixtures

[17] Published by John Wiley and Sons in 1917.

[18] The data are those of Young given in "Fractional Distillation," 1903, p. 151:

x	y	x	y
0.50	0.714	0.20	0.385
0.45	0.672	0.15	0.306
0.40	0.625	0.10	0.217
0.35	0.574	0.05	0.116
0.30	0.517	0.00	0.000
0.25	0.455		

of benzene and toluene with precision. This equation was derived by application of a modification of Formula 11 on p. 38 of Dr. Running's book.

Likewise the equation $y = 65.8 + 14.4(3.111)^x$ represents the relationship between composition of liquid and vapor and boiling point for any mixture of benzene and toluene when the total pressure is 760 mm. This was derived by application of formula 6 on page 28 of "Empirical Formulas." [19]

Development of the Theory of Fractional Distillation.

The use of fractional distillation as a method of separating the components of liquid mixtures is based on the fact that the composition of the vapor is different from that of the liquid. This was recognized in a qualitative way and formed the basis of commercial operations long before a comprehensive theory of distillation was quantitatively formulated. The Coffee still was designed by Coffee [20] of Dublin in 1832 and used commercially. The use of simpler stills dates back almost to the dawn of history. On the other hand the mathematical theory of the distillation of binary mixtures in a column still was first developed by Sorel [21] in 1893. Other notable contributions to the theory of distillation are those of Barrell, Thomas, and Young,[22] S. Young,[23] Lord Rayleigh,[24] W. K. Lewis,[25] Rosanoff,[26] A. F. Dufton [27] and Hausbrand.[28]

These discussions have been limited in the main to binary systems, though Barrell, Thomas, and Young, and also Rosanoff,[29] discuss a ternary mixture.

A symposium on fractional distillation at the 63rd meeting of the American Chemical Society resulted in the preparation and publication of several interesting papers.[30] These are mainly adaptations from or extensions of, the theory of distillation as developed by W. K. Lewis, who in turn acknowledges his indebtedness to Sorel. While Lewis' theoretical treatment of the subject is essentially a simplification of that of Sorel he nevertheless deserves much credit for crystallizing the subject matter and presenting it in a useful and understandable manner.

The reader should not overlook the recent work of Robinson, en-

[19] These equations were derived by Mr. John C. Geniesse in the course of work in progress in the Chemical Engineering Laboratories at the University of Michigan.

[20] "Chemistry as Applied to the Arts and Manufactures," Volume 1, Alcohol.

[21] "La Rectification de l'alcohol," Paris, 1893.

[22] *Phil. Mag.*, 37 (1894), 8.

[23] *J. Chem. Soc.*, 75 (1899), 679-710.

[24] *Phil. Mag.*, 4 (1902), 527.

[25] *J. Ind. Eng. Chem.*, 1 (1909), 522-33.

[26] *J. Am. Chem. Soc.*, 36 (1914), 2000-4; 37 (1915), 301-4.

[27] *Phil. Mag.*, 4 (1921), 633-46.

[28] *Die Wirkungsweise der Rektifizier und Distillier-Apparate*, 4th Edition—1921.

[29] *J. Am. Chem. Soc.*, 37 (1915), 1072-78.

[30] *J. Ind. Eng. Chem.*, 14 (1922), 476-97.

titled "The Elements of Fractional Distillation," which is an exposition of the Sorel-Lewis treatment of the subject, nor that of Young, which is a revised and much enlarged edition [31] of his well known "Fractional Distillation."

The Ideal Process of Fractional Distillation.

Fractional distillation as a method for producing changes in the composition of liquid mixtures or for separating the components of mixtures of Type I, is based on the fact that when a liquid mixture is heated and vaporized, the vapor is richer than the liquid in the more volatil component. The ideal distillation process at constant pressure consists in countercurrently contacting the upward flowing vapor and the downward flowing liquid so intimately that equilibrium between the two phases is obtained at all points, and change in composition of the phases occurs continuously. The ascending vapor becomes richer, and the descending liquid poorer, in the more volatil component. Temperature varies, and is dependent upon phase compositions at any point. An almost infinite number of successive and mutually dependent changes in composition occur. The ideal distillation process may be regarded as truly differential in nature. A heat loss is involved that depends on the weight of pure liquid B necessarily returned to the fractionating system.

Two types of ideal process must be considered, Type A, the process in which a definite part of the heat loss occurs in the apparatus for countercurrently contacting vapor and liquid, and Type B, the process in which the entire heat loss occurs in the reflux or partial condenser that returns liquid to the contacting apparatus.

The ideal system without reflux condensation is not made the basis of commercial operations and will therefore not be considered. The theory of this system has been developed by Lord Rayleigh [32] and by Rosanoff.[32a]

The discussion that follows will be limited to solutions or binary mixtures of substances A and B.

Distillation Process and Apparatus.

The nature of the ideal distillation process has just been indicated. The apparatus for conducting this hypothetical process would consist of a still, a column of infinite number of sections each designed to give perfect countercurrent contacting of liquid and vapor, a reflux to condense part of the vapor of the volatil component and return it to the top of the column, and a condenser to change the product from vapor to liquid. The commercial column differs from the ideal column in that it consists of a few sections only, and in other respects that will be indicated in the discussion that follows.

[31] New edition, 1922, published by Macmillan.
[32] *Phil. Mag.* (6), 4 (1902), 521-37.
[32a] *J. Am. Chem. Soc.*, 36 (1914), 2000-4.

In the design of commercial equipment for fractional distillation, and in the conduct of efficient fractional distillation operations, it is necessary to know:

1. The minimum weight of vapor that must be formed in the still at any time in order to separate unit weight of product at that time.

2. The minimum weight of reflux (i.e., weight of liquid returned to the top of the column) that must be returned to the top of the column at any time in order to separate unit weight of product at that time in a column designed to operate without heat loss.

3. The number of "perfect contacts" required to produce a given change in composition at any time, and for any given weight of reflux.

4. The number of "imperfect contacts" required to produce a given change in composition at any time, and for any given weight of reflux.

The paragraphs that follow will be devoted to methods for calculating these various quantities. The discussion will be limited at first to "batch" distillation and then will be extended to cover continuous distillation.

Diagram and Nomenclature.

The discussion that follows will be based on the diagram shown in Figure 14, and refers to the process of Type B in which the heat loss occurs entirely in the reflux. The apparatus consists of a still, a column that may be considered as made up of contacting sections or of unit lengths of packing or filling, a reflux or partial condenser, and a condenser that converts the product from vapor to liquid. The nomenclature is indicated on the diagram. It will be noted that each symbol is the initial letter of the name of the thing for which it stands. This scheme of nomenclature has the important advantage of clarity and avoidance of confusion. Each equation or expression can be readily expanded into words as it is read because of the ease with which initial letters are associated with the words for which they stand. It is only necessary to remember the following facts:

"C" always stands for a composition expressed in terms of the more volatil component and as a decimal part of unity. Physical units of weight and not mols are referred to. Except when used as subscripts

"L" always stands for a weight of liquid.

"V" always stands for a weight of vapor.

Subscripts:

Subscripts of "L" or "V" indicate the point in the apparatus where the particular weight of liquid or vapor is located.

Subscripts of C consist of two parts, first, a letter "L" or "V," indicating whether the composition is that of liquid or vapor, and second, letters S, N, R, P, etc., indicating the location of the liquid or vapor whose composition is referred to, as still,

n^{th}-plate, reflux, product, etc. The initial letter "P" for product has been used, rather than "C" for condenser, in order to avoid confusing such a "C" with the "C" standing for compositions.

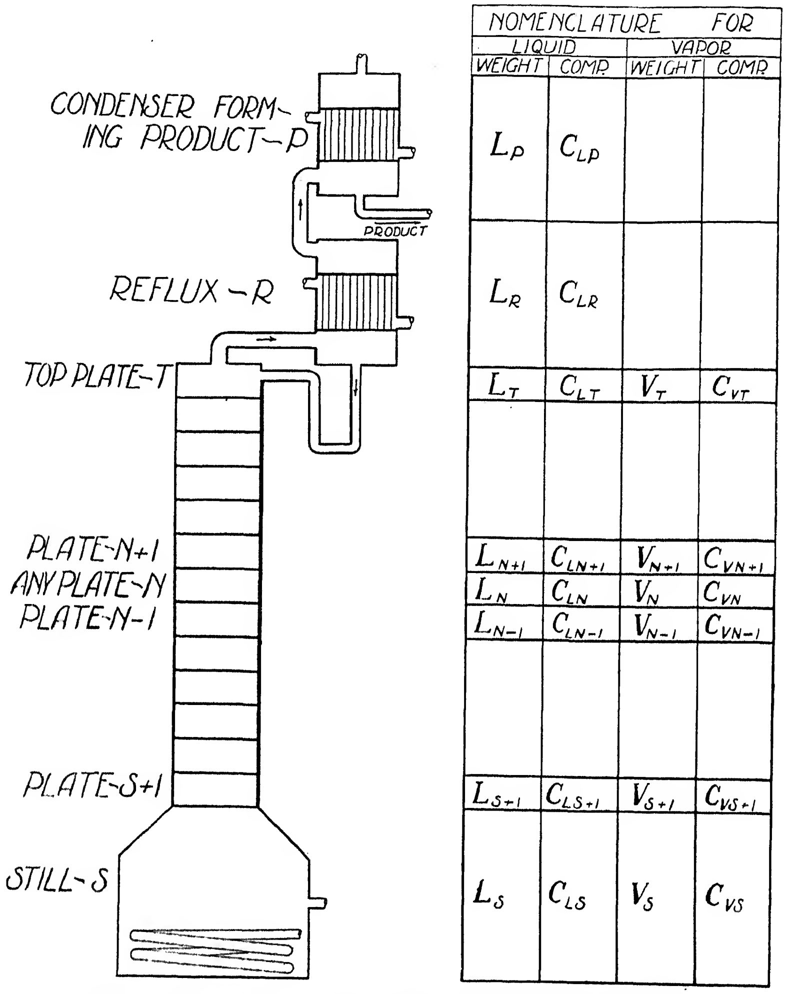


FIG. 14.—Diagram of Batch-Still Showing Nomenclature.

Other Symbols:

Symbols M_A, M_B, etc., stand for the molecular weight of the component indicated by the subscript.

Symbols h_a and h_b stand for the latent heats of vaporization per unit weight of substances A and B respectively.

Symbols H_A and H_B stand for the molal latent heats of vaporization of substances A and B respectively.
The mark ′, or "prime," indicates that the quantity so marked is the minimum. For example "L'_R" stands for the minimum weight of refluxed liquid.

Minimum Vaporization.

In order to separate a weight of product L_P from a binary mixture of substances A and B a weight of vapor V_S must be formed in the still. It is apparent that

$$V_S = L_P + L_{S+1} \tag{7}$$

in which L_{S+1} is the weight of the liquid returned to the still from the bottom of the column. Then, equating the weight of volatil component in the still-vapor to the weight of volatil component in L_P and L_{S+1}

$$V_S C_{VS} = L_P C_{LP} + L_{S+1} C_{LS+1} \tag{8}$$

Eliminating L_{S+1} from (7) and (8),

$$V_S C_{VS} = L_P C_{LP} + (V_S - L_P)\ C_{LS+1} \tag{9}$$

In an ideal fractionating apparatus operating with minimum reflux $C_{LS+1} = C_{LS}$. This can be seen from the following facts. If all the vapor from the still were condensed in the reflux, the weight and composition of the liquid returned to the still from the bottom of the column would be the same as the weight and composition of the vapor leaving the still, i.e., $L_{S+1} = V_S$, and $C_{LS+1} = C_{VS}$. Under these conditions the weight of liquid to be vaporized in the still in order to separate unit weight of product is infinite. However, to operate with total or maximum reflux is manifestly out of the question. Now as the weight of reflux used is decreased from this impractical maximum to amounts usual in commercial practice, and beyond that to the theoretical minimum, the weight of liquid necessarily formed in the still to separate unit weight of product is correspondingly decreased. Obviously C_{LS+1} is less than C_{VS} except when all vapor is condensed in the reflux. The less the weight of refluxed liquid the smaller is C_{LS+1}. But C_{LS+1} can never be less than C_{LS}, for it is apparent that it would never be possible by any process of countercurrent contacting to form from the still-vapor a liquid poorer in the volatil component than the liquid in equilibrium with the still-vapor. Hence C_{LS+1} always lies between the compositions C_{VS} and C_{LS}. As the reflux is decreased to a minimum C_{LS+1} approaches C_{LS} as a limit. When the reflux is minimum

$$C_{LS+1} = C_{LS} \tag{10}$$

This is the case now under discussion. Hence, combining (9) and (10), and solving for V'_S [33]

$$V'_S = \frac{L_P\ (C_{LP} - C_{LS})}{C_{VS} - C_{LS}} \qquad (11)$$

By the use of equation (11) the weight of vapor V'_S that must be formed in the still, in order to separate a weight L_P of product, can be calculated. It is important to remember that the weight V'_S found in this manner is the minimum vaporization, and applies only to operations conducted in the ideal apparatus with its infinite number of perfect contacts between vapor and liquid in the column. In any commercial apparatus the weight of liquid vaporized in the still is necessarily greater than the quantity V'_S calculated from equation (11). The calculation of the quantities in a commercial still are discussed below.

Minimum Weight of Reflux.

Distillation to be most economical in any given apparatus must be conducted with the least possible expenditure of heat energy per unit weight of product. Loss of heat in the ideal distillation system of Type B occurs entirely in the reflux and condenser. The loss in the condenser cannot be avoided as it is inherent in change of state from vapor to liquid. If the apparatus is to be economically operated, the heat loss in the reflux must be reduced to a practical minimum, approaching as nearly as may be feasible to minimum reflux in the ideal distillation apparatus. The ideal fractionating column consists of an *infinite number* of sections, each of which produces an *infinitesimal* change in phase compositions, whereas the commercial apparatus consists of a limited number of sections each of which must produce a *large* change in phase compositions. To effect such changes of compositions in commercial apparatus, it is necessary to increase the weight of liquid returned to the top of the column from the reflux, to weights generally greatly in excess of the minimum required in the ideal column.

In order to calculate the minimum weight of reflux in the ideal column, one must determine the minimum weight of vapor necessarily formed in the still per unit weight of product. The procedure for this has been developed, and the minimum vaporization can be calculated from equation (11).

From equation (7)

$$L'_{S+1} = V'_S - L_P$$

in which L'_{S+1} is the minimum weight of liquid returned to the still from the bottom of the column, and V'_S the minimum vaporization.

The minimum reflux L'_R cannot be calculated without taking into

[33] V'_S it will be recalled is used to designate the minimum V_S.

account the thermal quantities involved in composition changes in the column. An exact analysis, taking into account thermal quantities other than latent heats and heats of chemical reactions, requires data that are not available and is so involved as to be impractical. The error resulting from neglect of heat quantities other than these is well within the reasonable limits of accuracy in the design of commercial column apparatus.

A general relationship giving the approximate value of any L_R can be derived. In the following derivation only latent heats will be taken into account, since chemical reactions do not occur in the distillation operations of the oil-refinery except when heavy oils are distilled or when cracking is intended. Equating weights of liquids and vapors entering and leaving the column,

$$V_S + L_R = V_T + L_{S+1} \tag{12}$$

Equating latent heats of vapors entering and leaving the column

$$V_S C_{VS} h_b + V_S\ (1 - C_{VS})\ h_a \underset{\text{approx.}}{=} V_T C_{VT} h_b + V_T\ (1 - C_{VT})\ h_a \tag{13}$$

in which it will be recalled h_b = latent heat per unit weight of the more volatil component, and h_a = latent heat per unit weight of the less volatil component. These latent heats of vaporization are to be taken at the approximate mean temperature in the column.

But
$$V_T = L_P + L_R \tag{14}$$

Combining (13) and (14), and solving for L_R,

$$L_R \underset{\text{approx.}}{=} \frac{V_S\ [C_{VS}(h_b - h_a) + h_a]}{C_{VT}\ (h_b - h_a) + h_a} - L_P$$

and since C_{VT} equals C_{LP},

$$L_R \underset{\text{approx.}}{=} \frac{V_S\ [C_{VS}(h_b - h_a) + h_a]}{C_{LP}\ (h_b - h_a) + h_a} - L_P \tag{15}$$

Equation (15) is general and may be applied in ascertaining the value of L_R in the commercial column as well as in the ideal column. It may be applied equally well to the calculation of relationships in systems composed of A and B when these substances form concentrated perfect solutions or when they do not form such solutions. If A and B form a perfect solution the following relationships must hold

$$L_R \underset{\text{approx.}}{=} \frac{V_S\ [C_{VS}(M_A - M_B) + M_B]}{C_{LP}(M_A - M_B) + M_B} - L_P \tag{16}$$

in which M_A and M_B stand for the molecular weights of A and B respectively.

Equation (16) is somewhat more convenient than equation (15)

since molecular weights are always known even though latent heats may not be known. However, equation (16) can be applied only in those cases in which A and B form a perfect solution. Furthermore, when data are available, equation (15) should be used in preference to (16) because equation (16) is based on the assumption that molecular latent heats of A and B are equal.

If the minimum weight of reflux L'_R is desired, it may be calculated by substituting the minimum vaporization V'_S for V_S in either equation (15) or (16).

Change in Phase Compositions Per Unit Section of the Column.

In the design or operation of any column it is essential to know the change in composition of liquid and vapor that occurs in any unit section of the column, as well as in the entire column composed of any number of unit sections. A column section may be any number (not necessarily integral) of plates of any type, as for example bubbler-cap or sieve-plate, or it may be any arbitrarily chosen length or packed- or filled-column. The following treatment of the subject will not be concerned with the ideal column since this column is composed of an infinite number of sections in each of which an infinitesimal change of phase compositions occurs. The column consisting of a limited number of sections, in each of which equilibrium is established between vapor and liquid phases, will first be considered, and following this the commercial column with its limited number of sections and imperfect contact of vapor and liquid will be discussed. By "perfect" contacting is meant that type of contacting of vapor and liquid that results in establishing equilibrium. "Imperfect" contacting is any type of contacting that does not result in establishing equilibrium.

The column-section that produces the same change in compositions of vapor and liquid phases as is produced in one perfect contacting will be designated as a "perfect" column-section, or for brevity as a "perfect"-section. I have already pointed out that in any column of limited number of sections the change in phase-compositions per section must be finite, and must be large if the change in compositions in the entire column is large.

The symbol ΔC will be used to refer to the increment of change in composition from one section of the column to the next. The subscripts "L" or "V" will indicate whether the symbol for the increment refers to liquid or vapor. Thus ΔC_{LN} refers to the increment of change in composition of the liquid as a result of contact of liquid with vapor in the Nth section.

An exact relationship from which Δ_{CL} in any section of the column can be calculated is derived by equating the weights of materials entering and leaving suitably selected portions of the distillation system. The method of procedure is illustrated by the following development of an expression for ΔC_{LN}. It should be noted that the weight balances are so chosen that the final expression contains only known or

calculable weights and compositions. The derivation here given refers to batch distillation in an apparatus similar to that shown diagrammatically in Figure 14. Consider the column to be cut between sections N and N + 1. Then equating weights of materials

$$V_N = L_{N+1} + L_P \tag{17}$$

Likewise equating weights of the volatil component,

$$V_N C_{VN} = L_{N+1} C_{LN+1} + L_P C_{LP} \tag{18}$$

By definition of ΔC

$$\Delta C_{LN} = C_{LN+1} - C_{LN} \tag{19}$$

Combining (18) and (19) to eliminate C_{LN+1},

$$V_N C_{VN} = L_{N+1} (C_{LN} + \Delta C_{LN}) + L_P C_{LP}$$

Solving for ΔC_{LN},

$$\Delta C_{LN} = \frac{V_N C_{VN} - L_P C_{LP}}{L_{N+1}} - C_{LN} \tag{20}$$

Combining (17) and (20) to eliminate L_{N+1},

$$\Delta C_{LN} = \frac{V_N(C_{VN} - C_{LN}) - L_P(C_{LP} - C_{LN})}{V_N - L_P} \tag{21}$$

In equation (21) L_P, C_{LP}, and C_{LN} are known. C_{VN} is also known, for the perfect column-section, since it is the composition of the vapor in equilibrium with the liquid in the Nth section. V_N may be assumed, but more commonly L_R per unit weight of L_P is assumed, and V_N approximately calculated by taking into account heat quantities as in equation (15). The relationship applicable in this case is

$$V_{N \atop \text{approx.}} = \frac{(L_R + L_P)\ [C_{LP}(h_b - h_a) + h_a]}{C_{VN}(h_b - h_a) + h_a} \tag{22}$$

The approximate equation (22) may be derived by substituting C_{VN} for C_{VS}, and V_N for V_S, in equation (15), and solving for V_N.

When A and B form concentrated perfect solutions it follows from equation (16) that equation (22) may be written

$$V_{N \atop \text{approx.}} = \frac{(L_R + L_P)\ [C_{LP}(M_A - M_B) + M_B]}{C_{VN}(M_A - M_B) + M_B} \tag{23}$$

Calculation of the Number of Perfect Sections Required in a Column.

In the foregoing paragraphs a method has been formulated for calculating the change in phase compositions in one perfect column-

section. The relationship of ΔC_{LN} to known weights and compositions of liquids and vapors in any section "N" is given by equations (21) and (22).

The general problem of calculating the number of perfect column sections required to produce any desired change in phase compositions in a system of two components, when operating with a given ratio of weight of reflux to weight of product, can now be solved.

The procedure is as follows:

a. Construct the isobaric curve showing the composition of the vapor in equilibrium with liquid of any composition, that is, the curve showing the relationship between composition of liquid C_L and vapor C_V at constant pressure.

b. Using equation (22) calculate the value of V_N corresponding to a series of arbitrarily selected values of C_{LN}. Construct a $V_N \sim C_{LN}$ curve from which values of V_N may be read for any value of C_{LN}.

c. Find the value of the first ΔC_L by substituting values of the quantities V_N, L_P, C_{VN}, C_{LN} and C_{LP}, all of which are known or found as in (a) and (b). The first change in composition occurs in the still, which should really be regarded as the first section of the column.

d. Add the value of ΔC_L found in (c) to the value of C_L used in (c), which in this first instance is C_{LS}. This sum is the composition of the liquid in the next perfect column-section which, in this instance, is the bottom perfect-section of the column.

e. Using this new value of C_L, calculate ΔC_L for the first perfect-section by a repetition of the processes above outlined. The sum of this C_L and ΔC_L is the composition of the liquid in the second perfect-section.

f. Repeat the calculations in like manner until the sum of C_L and ΔC_L is equal to or exceeds the desired composition of the product C_{LP}. The number of perfect-sections required will then be apparent.

The foregoing method of calculating the number of perfect column-sections required to produce a given change in liquid composition is satisfactory when the number of sections required is small. The number of perfect-sections will be small if the corresponding values of C_L and C_V are widely different, and if the total change in composition to be effected is small.

If the number of sections required is large the foregoing method of calculation is tedious. Consequently, if it is apparent that the number of sections required may be large the following method involving graphic integration will be found convenient. This method is best illustrated by a specific problem.

Statement of the Problem.

A solution containing benzene and toluene is to be distilled in such a manner as to give a product containing 95 per cent of benzene by

weight. At the instant when the liquid in the still contains 20 per cent of benzene and 80 per cent of toluene by weight it is desired to know the minimum number of perfect column sections that will be required if the ratio of weight of reflux to weight of product is 4: 1. Pressure throughout the system is assumed to be 750 mm. of mercury.

Solution of the Problem.

The first step in the solution of the problem is the construction of the isobaric diagram showing the composition of the vapor in equi-

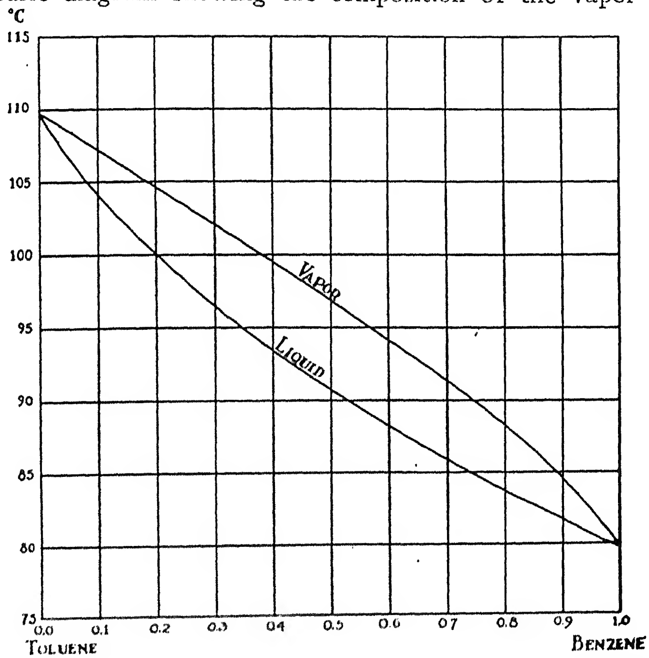


FIG. 15.—Boiling Point ~ Composition Diagram for the System Benzene-Toluene at 750 mm.

librium with solutions of benzene and toluene of any composition. The curves marked "liquid" and "vapor" in Figure 15 give the necessary information. Columns 1 and 2 in Table XXI show equilibrium values of liquid and vapor compositions as read from these curves.

The second step is to calculate values of V_N corresponding to arbitrarily selected values of C_{VN}. For this purpose appropriate values are substituted in equation (22) or (23). In this instance equation (23) is used since benzene and toluene form a solution that may be regarded as approximating to the concentrated perfect solution. The following illustrates the method of making the calculation.

TABLE XXI

VALUES OF QUANTITIES REQUIRED FOR SOLUTION OF BATCH-DISTILLATION PROBLEM

C_{LN}	C_{VN}	V_N	ΔC_{LN}	$\frac{1}{\Delta C_{LN}}$
0.20	0.375	5.48	0.0467	21.37
0.25	0.445	5.42 a	0.0806	12.42
0.30	0.508	5.36 a	0.1080	9.27
0.40	0.620	5.26	0.1424	7.03
0.50	0.714	5.19 a	0.1574	6.36
0.60	0.792	5.126	0.1538	6.50
0.70	0.857	5.07 a	0.1340	7.47
0.80	0.913	5.027	0.1038	9.64
0.90	0.960	4.99 a	0.0626	15.98
0.95	0.980	4.978	0.03757	26.62

a. Read from $C_{LN} \sim V_N$ curve, Fig. 16.

The first arbitrarily selected value of C_{VN} is 0.375, corresponding to a liquid composition 0.20.

$$V_N = \frac{(L_R + L_P)\ [C_{LP}(M_A - M_B) + M_B]}{C_{VN}(M_A - M_B) + M_B} \quad \text{eq. (23)}$$

$$V_N = \frac{(4 + 1)\ [0.95(92 - 78) + 78]}{0.375(92 - 78) + 78} = 5.48$$

The values of V_N shown in column 3 of Table XXI were calculated in similar manner. The $C_{LN} \sim V_N$ curve plotted from these data is shown in Figure 16.

The third step is to calculate values of ΔC_{LN} corresponding to arbitrarily chosen values of C_{LN}. This may be done by substituting proper values in equation (21). Values of V_N can be read from the $C_{LN} \sim V_N$ curve of Figure 16.

$$\Delta C_{LN} = \frac{V_N(C_{VN} - C_{LN}) - L_P(C_{LP} - C_{LN})}{V_N - L_P} \quad \text{eq. (21)}$$

For the perfect section in which the composition of the liquid is 0.20

$$\Delta C_{LN} = \frac{5.48(0.375 - 0.20) - 1.00(0.95 - 0.20)}{5.48 - 1.00} = 0.0467$$

The values shown in column 4 of Table XXI were calculated in similar manner.

The values of ΔC_{LN} are the changes in composition in one perfect column-section. The reciprocals of these values are the number of perfect column-sections required to produce unit change in liquid composition at the point in the column where, in one section, the composition of the liquid changes from C_{LN} to $C_{LN} + \Delta C_L$, when the

composition of the product is C_{LP}. Values of $\frac{1}{\Delta C_{LN}}$ are shown in column 5 of Table XXI.

The fourth step in the solution of the problem is the graphical integration of $\frac{1}{\Delta C_{LN}} \cdot C_{LN}$ between desired limits which in this problem are 0.95, i.e., the composition of the product, and 0.20, i.e., the composition of the liquid in the still. In order to accomplish this graphical integration it is necessary to construct a curve of the type

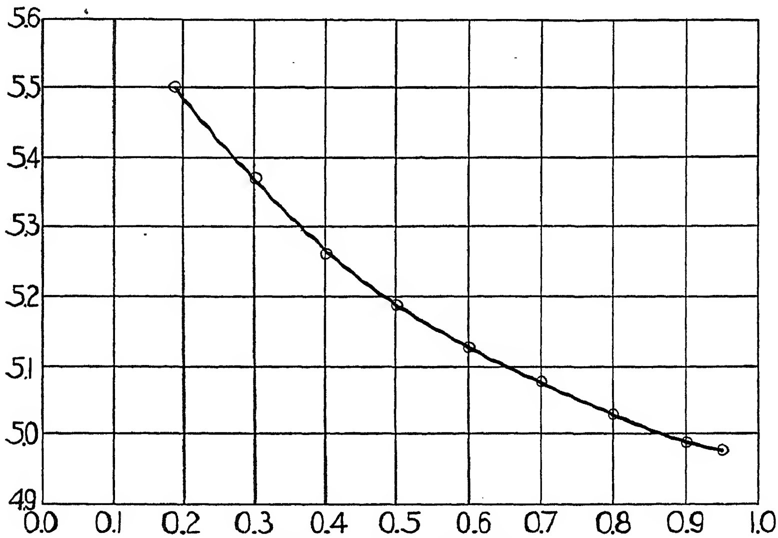
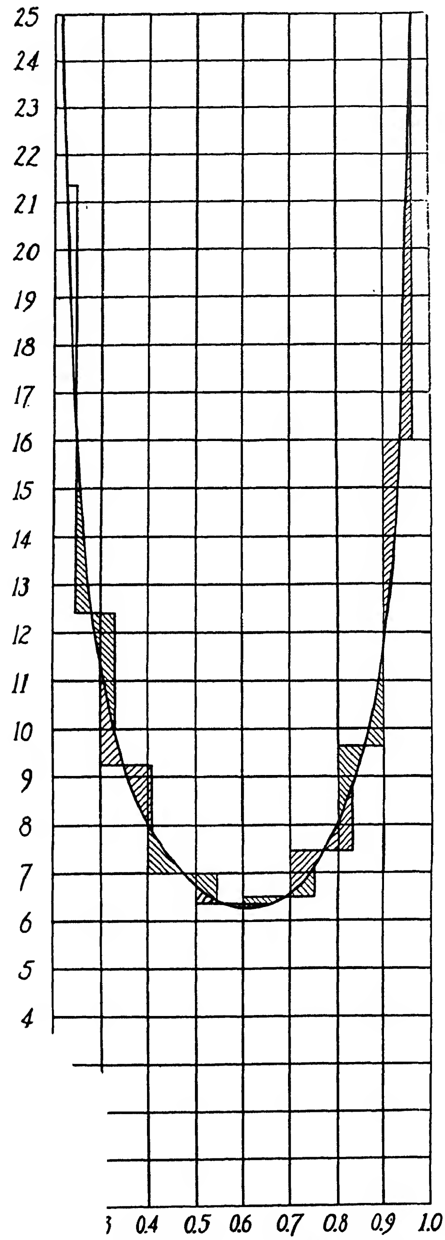


FIG. 16.—$C_{LN} \sim V_N$ Curve.

shown in Figure 17. The first step in obtaining this curve is to plot horizontal lines of length of the ΔC_{LN} corresponding to the selected values of C_{LN} and at distances from the horizontal axis equal to the corresponding value of $\frac{1}{\Delta C_{LN}}$. The abscissas of the ends of each horizontal line are thus C_{LN} and $(C_{LN} + \Delta C_L)$. The smooth curve shown in Figure 17 is so drawn that the area under the curve between the abscissas corresponding to the ends of any of the horizontal lines is equal to the area under that horizontal line. The area under any of the horizontal lines is a rectangle whose dimensions are ΔC_{LN} and $\frac{1}{\Delta C_{LN}}$, and whose area is therefore 1.0. The curve shown in Figure 17 is so drawn that the similarly shaded areas above and below any horizontal line are equal. It should be noted that only occasionally will the smooth curve bisect a horizontal line. A planimeter will be found most helpful in constructing the smooth curve.



7.—Curve for integration of $\frac{1}{\Delta C_{LN}} \cdot C_{LN}$

The value of the desired integral is the area bounded by the smooth curve, the horizontal-axis, and the ordinates drawn through abscissas 0.20 and 0.95. The smooth-curve has not been extended to intersect the ordinate 0.20 as this was in this instance both inconvenient and unnecessary, since the area under the smooth curve between the abscissas 0.2 and (0.2 + 0.0467) must be 1.0. The area under the curve between abscissas 0.2467 and 0.95 is 6.005. The total area is 7.005, and therefore the number of perfect column sections required to change the composition from 0.20 to 0.95 is seven. As has been noted, one of these sections is the still itself, and therefore the number of perfect sections in the column is six.

The General Problem of Batch Distillation.

The problem that has just been outlined and the solution presented exemplify the method of attack on the general problem of the design of apparatus for batch distillation. In general, it will be desired to accomplish separations by distillation at the lowest possible cost. This entails a proper balancing of fixed or overhead charges and direct operating costs, or, in other words, an optimum relationship between the number of perfect sections in the column and the average reflux-ratio. So, in the design of column-apparatus, it is necessary not only to provide a number of sec-

tions that will allow the required separation, but also to take into account the cost factors.

The variables in the design of a column for separating the components of any given solution are those of equations (21) and (22) namely:

1. Composition of product.
2. Composition of liquid in still at any instant.
3. The reflux-ratio, which equals $\dfrac{\text{Weight of Reflux in unit time}}{\text{Weight of Product in unit time.}}$
4. The number of perfect column sections.
5. The weight of the product.

Since the present discussion is concerned with the separation of the components of a particular solution the quantities representing inherent properties of the system do not enter the discussion as variables. The equilibrium values of liquid and vapor compositions are determined by the nature of the substances composing the given solution.

The number of column-sections required to make a given change in compositions will be smaller the larger the numerical difference of the equilibrium values of composition of liquid and vapor, that is, the quantity $C_V—C_L$. Inspection of the isobaric diagram will render apparent the fact that the composition difference $C_V — C_L$ is small when C_L approaches the composition of either substance or that of any constant-boiling mixture. Hence, the less pure the product the smaller is the necessary number of perfect sections required for the separation. Also, the larger the proportion of the volatil component in the liquid in the still at any instant, the fewer the sections needed to effect the separation. Since in batch distillation the composition of the liquid in the still continuously changes, it is desirable to make calculations, similar to that given in detail above, for several successive compositions of the still-liquid.

The column may be designed to operate with any reflux-ratio greater than the minimum reflux-ratio for any composition of the still-liquid. The larger the reflux-ratio the smaller the number of perfect sections required to effect any desired separation. Hence, for each of the several compositions of the still-liquid it is desirable to calculate the number of perfect column-sections for each of a series of assumed reflux-ratios.

When the foregoing calculations have been made the designer is in a position to select the number of perfect sections for the column, and to specify the smallest reflux-ratio that can be used for any composition of still-liquid. Rather than attempt difficult separations that necessitate the use of an unduly large number of perfect column-sections, or of an excessive reflux-ratio, it will be found desirable to separate an intermediate fraction of composition much smaller than that of the product. The weight of this fraction which must be

redistilled will not be large. It will be more economical to proceed in this manner than to construct and operate the still so as to make possible the nearly quantitative separation of the given solution into desired product and residue.

The factors discussed in the foregoing paragraphs condition the design of the column as to number of perfect sections, but not as to its capacity. The capacity or horizontal cross-sectional area is dependent on the weight of product to be made in unit time. The weight of product and the largest reflux-ratio determine not only the cross-sectional area of the column, but also the area of the heating surfaces in the still, the cooling surface of reflux and condenser, and the sizes of the piping.

Relation of the "Perfect" Column-Section to the Plate or Unit-Length of the Working Column.

The foregoing discussion of the calculation of the number of column-sections required to produce a given change in composition has been based on the conception of the "perfect" column-section, that is, the section into which liquid and vapor of any composition may enter and in which they are so brought into contact that equilibrium is established. In order that the equations developed can be used in the design of distillation apparatus it is necessary to establish relationships between the "perfect" column-section and the plate or unit-length of columns used in practice.

The plate or unit-length of the working column is ineffective in producing equilibrium for two reasons:

1. Liquid and vapor are not brought into sufficiently intimate contact.
2. The time of contact is necessarily too short.

Obviously, the molecules of liquid and vapor cannot be brought together with the required intimacy of contact in the time allotted and by a physical process so crude that it involves proximity of drops and bubbles rather than admixture of particles of molecular dimensions.

Were equilibrium established the number of molecules of A and also of B entering the liquid from the vapor and entering the vapor from the liquid would be equal. This is equivalent to the statement that the vapor tension of each component in the liquid would be equal to the vapor pressure of the same component in the vapor, or again, the difference in pressures of each component in the two phases would be zero. The rate at which equilibrium is approached in any system is dependent on the magnitude of the force or forces tending to bring the system into equilibrium. The forces in this instance are the differences in pressures of each component in the two phases. As equilibrium is approached these forces approach zero, and consequently the rate of approach to equilibrium becomes continuously less. In commercial practice advantage must be taken of the rapid rate of

change resulting from large pressure differences operative at the beginning of the process that if completed, would result in establishing equilibrium.

As a result of the fact that a commercial column must produce a reasonable quantity of product in any given time, the rate of change of phase-compositions must be rapid, or the time required for a given change must be small. If the time required is large the column must be large, and the loss of heat also excessive. Even if liquid and vapor were brought into most intimate contact in a working-column it would be impractical so to operate the column as to reach equilibrium in any section.

Because of lack of intimate contact, diffusion of the components in each phase is also involved in the processes in progress in every section. Rate of diffusion is dependent, among other factors, on the difference of pressures of each component in both phases. A high rate of diffusion is necessary to compensate in some measure for lack of intimacy of contact of the phases.

As a consequence of the fact that equilibrium is not established at any point in a working column this column must be composed of more sections than the "perfect" column. Some number (not necessarily integral) of plates or unit-lengths of the working column will produce the same change in compositions as one perfect column-section. This equivalent number is not always the same, but is dependent on velocity of flow of liquid and vapor, in the column, and on diffusion velocities of the components. Temperature and pressure affect the velocities of both flow and diffusion.

The technical literature contains very few references to measurements of phase compositions in working columns. In a recent article [34] W. K. Lewis calculates from rather incomplete data given by Mariller [35] that in the distillation of a water-alcohol mixture 1.1 plates of a working-column were equivalent to one perfect column-section. W. A. Peters [36] reports the results of experiments which indicate that when a mixture of acetic acid and water is distilled in a 28-inch diameter sieve-plate column of 28 plates, the number of plates equivalent to one perfect column-section is nearly the same as when this solution is distilled through a 4⅞-inch bubbler-cap plate-column of 20 plates with one bubbler-cap on each plate, the numbers being 1.92 plates and 2.22 plates respectively. When a solution of alcohol and water was distilled, in one instance through a 36-inch Badger bubbler-cap plate-column, and in another through the 4⅞-inch bubbler cap plate-column, the plates equivalent to one perfect-section were 1.43 and 1.44 respectively. Peters also reports the results of experiments conducted to determine the length of ring-packed laboratory column equivalent to one perfect column-section. His results are shown in Table XXII. The large influence of the nature of the substances composing the

[34] *J. Ind. Eng. Chem.*, 14 (1922), 496.
[35] "Distillation Fractionée."
[36] *J. Ind. Eng. Chem.*, 14 (1922), 476-9.

solution is evident. In each instance the column was packed with ¼-inch ring-filling.

The data in Table XXII show, in a general way, that the higher the molecular weight the larger the number of plates required to do the work of one perfect column-section. This is to be expected because of the dependence of rate of diffusion on molecular weight. Peters has also studied the effect of variation of ring size in the distillation of an acetic acid-water solution through a ring-packed laboratory column. The height of column equivalent to one perfect column-section was found to be roughly proportional to the diameter of the packing rings. His results are shown in Table XXIII.

TABLE XXII

LENGTHS OF RING-PACKED LABORATORY COLUMN EQUIVALENT TO ONE PERFECT COLUMN-SECTION

System Distilled	Height of Column Equivalent to One Perfect Column-Section Inches
Ethyl Alcohol-Water containing over 88% alcohol	4.2
Ethyl Alcohol-Water containing less than 88% alcohol	3.65
Ethyl Alcohol-Water, dilute Residue almost pure H_2O	3.87
Methyl Alcohol-Water	3.0
Acetone-Ethyl Alcohol	6.0
Nitric Acid-Water	8.0
Nitric Acid-Water-Sulfuric Acid	3.75
Acetic Acid-Water	10.0
Benzene-Toluene	10.0
Ammonia-Water Residue to be almost pure water	3.4

TABLE XXIII

RELATION OF RING-DIAMETER TO COLUMN EFFECTIVENESS

Diameter of Ring in Inches	Height of Column Equivalent to One Perfect Column-Section Inches
⅛	6.2
¼	10.0
½	11.3
⅝	23.6
1	52.5

Since the conception of the "perfect" column-section is so new, it is not surprising that the technical literature contains so little information regarding the effectiveness of various plates and unit column-sections in terms of the perfect column-section. One might expect, in view of the wide application of distillation, that information regard-

ing compositions of still-liquid, reflux, and product, and weights of vapor and product formed in given time intervals would be available for many systems. Data of this type could be used in calculating the over-all relationship between the perfect column-section and the plates or unit-sections of the working column for the given solution and conditions of operation.

From the data covering alcohol-water solutions given by Peters and reproduced in Table XXIII it appears that the equivalence of the perfect-section and the working-plate does not vary greatly with the composition of the solution. Apparently, the over-all equivalence is roughly the same as that for any plate. It is not unreasonable to suppose that the equivalence noted here for the system alcohol-water may hold for other systems, but experimental verification is lacking.

For purposes of close design it is essential to know the equivalence of the perfect and working sections with some accuracy, but, if reasonable latitude is allowable in design, use may be made of rough values of the equivalence. Satisfactory values for any given solution can be determined by experiment using, as closely as possible, velocities of liquid and vapor that are to be employed in the apparatus to be constructed. If the new apparatus is to be used over a wide range of conditions it is only necessary to determine the equivalence under the most unfavorable working conditions. It may be argued that if experiment is required in each case to determine the relationship between the perfect and the working section the methods here presented are of little practical value. The answer to this is that experimental data covering the systems commonly distilled will soon be available. In the meantime the use of a reasonable factor of safety in applying such information as is available, or may be obtained by simple experiment, will permit fairly satisfactory design. In this connection, it should be kept in mind that if data are available for a system such as ethyl-alcohol-water, this may prove a useful guide in the design of equipment for the distillation of propyl alcohol-water. Likewise data for solutions of benzene and toluene may be applied for toluene-xylene.

A further extension of the general method of design given in this chapter lies in the design of equipment for such separations as are involved in re-running gasoline, and in separating natural-gasoline from absorption oil. In these cases a solution of many hydrocarbons is separated into a volatil mixture and a less volatil residue. The residue may be regarded as component A and the distillate as component B of a binary mixture. The difficulty here arises in expressing the composition of residue and product as a decimal part of unity. The theoretical and analytical aspects of this subject are now being studied in the Chemical Engineering Laboratories at the University of Michigan.

The crude methods of distillation now in such general use in petroleum refineries bespeak the urgent need of consideration by refinery engineers of the fundamental principles of distillation. Many apparatus now in use would never have been built had the designers had

even so much as a clear qualitative understanding of basic principles. I shall have occasion to recur to this subject. The fallacious reasoning that since extremely sharp separations are not required in the preparation of petroleum products, almost any kind of plant equipment is good enough, has deadened the interest of engineers in fundamental theory and resulted in stagnation. The postulate is nonsense, for correctly designed apparatus is flexible, effective, and efficient, and will accomplish with ease what is now too often done with difficulty and at excessive cost.

Column Apparatus for Continuous Distillation.

The simplicity and economy with which the continuous still can be operated favor the use of this type of apparatus whenever feasible. All parts of the continuous apparatus work under constant conditions, whereas in batch distillation the conditions change continuously throughout the operation. The continuous still may be run at full capacity at all times, whereas in batch distillation the changing relationships prevent utilization of all parts of the apparatus at capacity at all times. Because of the fact that apparatus for continuous distillation operates under constant conditions, this type of equipment can be accurately designed.

The discussion that follows is concerned with the development of expressions for quantity of feed, minimum vaporization, weight of reflux, and change in composition effected by one perfect column-section located above or below the feed-plate. The equations developed in the preceding sections with reference to batch distillation give relationships between conditions and quantities at any instant. Similar expressions applicable to the phenomena of continuous distillation are complicated by the fact that solution (i.e., feed) is introduced at some point along the column. The section into which the feed is introduced is known as the "feed-section," or in the working column of the plate type as the "feed-plate." If a packed column is employed a plate for distributing the feed will commonly be used. The unit-section containing this plate will be designated in this instance also as the "feed-plate."

Nomenclature.

The nomenclature used in the discussion that follows will be the same as that of the preceding sections, with the following additions or modifications:

The subscript "F" refers to the feed and not to the feed-section.
The subscript "N" is reserved to designate the feed-section or any section above the feed-section.
The subscript "M" refers to the "mixing"- or feed-section. Sections above and below this may be designated by subscripts $M+1$, $M+2$, $M-1$, $M-2$, etc.

The subscript "B" refers to any section below the mixing- or feed-section. Sections above or below this may be designated by subscripts B + 1, B + 2, B — 1, B — 2, etc.

It should be noted that some sections in the column may be referred to by more than one subscript. The nomenclature used is shown in Figure 18 to which the discussion refers.

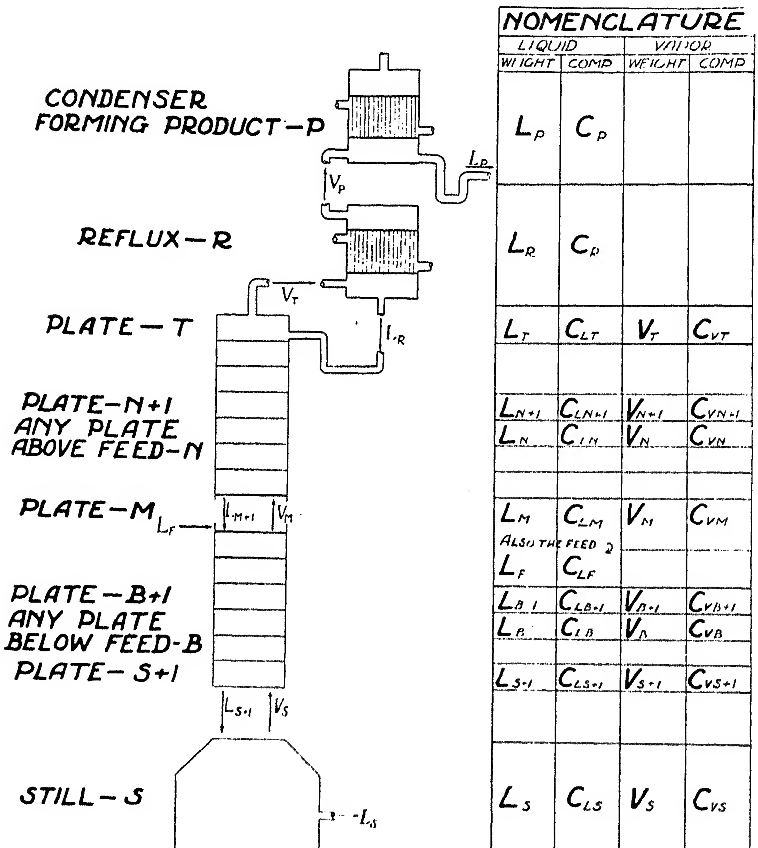


FIG. 18.—Diagram of Continuous Still Showing Nomenclature.

Quantity of Feed and of Residuum.

The liquid fed to the column in any given time must equal in weight the sum of the weights of product and liquid flowing from the still. Likewise, the weight of either component contained in the liquid fed to the column in any given time must equal the sum of the weights of this component in the product and residuum. That is,

$$L_F = L_P + L_S \tag{24}$$

$$L_F C_{LF} = L_P C_{LP} + L_S C_{LS} \tag{25}$$

Combining (24) and (25) to eliminate L_S,

$$L_F = \frac{L_P(C_{LP} - C_{LS})}{C_{LF} - C_{LS}} \tag{26}$$

Likewise, combining (24) and (25) to eliminate L_F,

$$L_S = \frac{L_P(C_{LP} - C_{LF})}{C_{LF} - C_{LS}} \tag{27}$$

Note that L_S is also equal to $L_F - L_P$.

Minimum Vaporization.

In order to separate a weight of product L_P from a binary mixture of substances A and B, a weight of vapor V_S must be formed in the still. However, since the vapor in this instance is not the source of all the volatil component entering the column, as was the case in the batch-still, it is necessary to take in account heat quantities as well as weights of volatil component entering and leaving the apparatus in order to formulate a relationship that can be solved for the minimum vaporization V'_S. The quantity V'_S is found by considering separately the portions of the column above and below the feed-section.

For the portion of the column above the feed-section it follows by analogy from equation (11) that

$$V'_M = \frac{L_P(C_{LP} - C_{LM})}{C_{VM} - C_{LM}} \tag{28}$$

The minimum vaporization V'_S can be expressed in terms of V'_M by taking into account the approximate equality of the heat in the vapor entering and leaving the portion of the column below, and including, the feed-section. By analogy, from equation (15)

$$V'_S \underset{\text{approx.}}{=} \frac{V'_M[C_{VM}(h_b - h_a) + h_a]}{[C_{VS}(h_b - h_a) + h_a]} \tag{29}$$

and, from equation (16)

$$V'_S \underset{\text{approx.}}{=} \frac{V'_M[C_{VM}(M_A - M_B) + M_B]}{[C_{VS}(M_A - M_B) + M_B]} \tag{30}$$

Combining equations (28) and (29) to eliminate V'_M

$$V'_S \underset{\text{approx.}}{=} \frac{[C_{VM}(h_b - h_a) + h_a] \cdot L_P(C_{LP} - C_{LM})}{[C_{VS}(h_b - h_a) + h_a] \ (C_{VM} - C_{LM})} \tag{31}$$

When reflux is a minimum, the number of perfect sections in the column is infinite and the change in composition from one section to

the next is infinitesimal. Hence, $C_{LM} = C_{LF}$ and $C_{VM} = C_{VF}$, for, were C_{LM} not equal to C_{LF}, a finite change in composition of liquid in the column would result from introduction of the feed. Such discontinuity in liquid composition in the column of infinite number of sections is impossible. Hence

$$V'_S \underset{\text{approx.}}{=} \frac{[C_{VF}(h_b - h_a) + h_a] \cdot L_P(C_{LP} - C_{LF})}{[C_{VS}(h_b - h_a) + h_a] \quad (C_{VF} - C_{LF})} \qquad (32)$$

In like manner from equations (28) and (30)

$$V'_S \underset{\text{approx.}}{=} \frac{[C_{VF}(M_A - M_B) + M_B] \cdot L_P(C_{LP} - C_{LF})}{[C_{VS}(M_A - M_B) + M_B] \quad (C_{VF} - C_{LF})} \qquad (33)$$

Equations (29), (30), (31), (32), and (33) hold if the feed is in liquid form, and at the temperature of the liquid in the feed-section. In the commercial practice of today the feed is seldom in vapor form, but, were such the case, equations could be developed that would take this additional factor into account.

Minimum Weight of Reflux.

When vaporization is a minimum, the weight of liquid returned to the still from the bottom of the column and also the weight of reflux are minimum. Equating weights of vapor and liquid entering and leaving the apparatus between the bottom of the column and the condenser

$$L'_{S+1} = V'_S + L_F - L_P \qquad (34)$$

combining equations (32) and (34)

$$L'_{S+1} \underset{\text{approx.}}{=} \frac{[C_{VF}(h_b - h_a) + h_a] \quad L_P(C_{LP} - C_{LF})}{[C_{VS}(h_b - h_a) + h_a] \quad (C_{VF} - C_{LF})} + L_F - L_P \qquad (35)$$

Equations (33) and (34) may be similarly combined to give an expression for the minimum weight of liquid leaving the bottom of the column.

The minimum weight of reflux is found as follows. Equating weights of materials in and out of the reflux

$$V_T = L_P + L_R \qquad (36)$$

Equating latent heats of vapors entering and leaving the column as was done in developing equation (13)

$$V_S C_{VS} h_b + V_S(1 - C_{VS})h_a \underset{\text{approx.}}{=} V_T C_{VT} h_b + V_T(1 - C_{VT})h_a \qquad (37)$$

Combining equations (36) and (37) to eliminate V_T

$$L_R \underset{\text{approx.}}{=} \frac{V_S[C_{VS}(h_b - h_a) + h_a]}{C_{VT}(h_b - h_a) + h_a} - L_P \qquad (38)$$

Since $C_{VT} = C_{LP}$

$$L_R \underset{\text{approx.}}{=} \frac{V_S[C_{VS}(h_b - h_a) + h_a]}{C_{LP}(h_b - h_a) + h_a} - L_P \qquad (39)$$

It should be noted that the vaporization (i.e., the quantity V_S in equation (39)) in the continuous still equals $L_P + L_{S+1} - L_F$ whereas in the batch still $V_S = L_P + L_{S+1}$.

An equation giving the value of L_R in terms of molecular weights rather than heats of vaporization may be written if the substances A and B form concentrated perfect solutions.

$$L_R \underset{\text{approx.}}{=} \frac{V_S[C_{VS}(M_A - M_B) + M_B]}{C_{LP}(M_A - M_B) + M_B} - L_P \qquad (40)$$

The derivation of equation (40) is similar to that of equation (16).

The minimum weight of reflux L'_R for the ideal column is calculated by substituting the minimum vaporization V'_S (calculated from equation (32) or (33)) in either equation (39) or (40).

Change in Phase Compositions Per Unit Section of the Column Above the Feed-Section.

The phenomena in the perfect continuous column above the feed-section are the same as in the column of a batch-still. The phase compositions and quantities in this portion of the continuous column are the same as those in the column of a batch-still when the composition of the liquid in the batch-still is the same as that in the feed-section of the continuous column. Consequently, equations (17) to (23) inclusive hold true for this portion of the continuous column and are rewritten below as equations (41) to (47) inclusive.

$$V_N = L_{N+1} + L_P \qquad (41)$$

$$V_N C_{VN} = L_{N+1} C_{LN+1} + L_P C_{LP} \qquad (42)$$

$$\Delta C_{LN} = C_{LN+1} - C_{LN} \qquad (43)$$

$$\Delta C_{LN} = \frac{V_N C_{VN} - L_P C_{LP}}{L_{N+1}} - C_{LN} \qquad (44)$$

$$\Delta C_{LN} = \frac{V_N(C_{VN} - C_{LN}) - L_P(C_{LP} - C_{LN})}{V_N - L_P} \qquad (45)$$

$$V_N \underset{\text{approx.}}{=} \frac{(L_R + L_P)\ [C_{LP}(h_b - h_a) + h_a]}{C_{VN}(h_b - h_a) + h_a} \qquad (46)$$

, when substances A and B form concentrated perfect solutions,

$$V_N \underset{\text{approx.}}{=} \frac{(L_R + L_P)\ [C_{LP}(M_A - M_B) + M_B]}{C_{VN}(M_A - M_B) + M_B} \qquad (47)$$

Change in Phase Compositions Per Unit Section of the Column Below the Feed-Section.

The phenomena below the feed-section in the perfect continuous column are the same as those above the feed-section, but the weights and compositions of the fluids are modified as a result of the introduction of the feed. Above the feed-section all descending liquid is condensed vapor, whereas below the feed-section the quantity of liquid resulting from the condensation of vapor is increased in some measure by the introduction of the feed. In developing an equation for the change in composition in one perfect section below the feed-section it is necessary to take this into account. Equating weights of liquid and vapor entering and leaving that portion of the column between the sections "B" and "M + 1,"

$$V_B + L_F + L_{M+1} = V_M + L_{B+1} \tag{48}$$

By definition of ΔC_L

$$\Delta C_{LB} = C_{LB+1} - C_{LB} \tag{49}$$

Equating weights of liquid and vapor entering and leaving the apparatus above the M^{th}-section,

$$V_M = L_{M+1} + L_P \tag{50}$$

Combining equations (48) and (50) to eliminate L_{M+1},

$$V_B + L_F = L_P + L_{B+1} \tag{51}$$

Equating the weights of volatil component in the quantities in equation (51),

$$V_B C_{VB} + L_F C_{LF} = L_P C_{LP} + L_{\ B+1\ LB+1} \tag{52}$$

Combining equations (49) and (52) to eliminate C_{LB+1},

$$V_B C_{VB} + L_F C_{LF} = L_P C_{LP} + L_{B+1}\ (\Delta C_{LB} + C_{LB})$$

Solving for ΔC_{LB},

$$\Delta C_{LB} = \frac{V_B C_{VB} + L_F C_{LF} - L_P C_{LP}}{L_{B+1}} - C_{LB} \tag{53}$$

Combining (51) and (53) to eliminate L_{B+1},

$$\Delta C_{LB} = \frac{V_B(C_{VB} - C_{LB}) + L_F(C_{LF} - C_{LB}) - L_P(C_{LP} - C_{LB})}{V_B + L_F - L_P} \tag{54}$$

From definition of subscript "B," the B^{th} section may be any section of the column below the feed-section, and may therefore coincide with the still, in which event $C_{LB} = C_{LS}$, and $C_{VB} = C_{VS}$.

The use of the above equations for the continuous column will presently be illustrated by a problem.

Location of the Mixing- or Feed-Section of a Continuous Column.

The principle that governs the choice of the section into which the feed should enter a continuous column is that this section shall be so selected that the number of sections required in the column shall be a minimum. The position of the feed-section is somewhat influenced by the reflux-ratio (i.e., $\frac{\text{Wt. of Reflux}}{\text{Wt. of Product}}$).

The feed-section of the ideal column with infinite number of sections is that section in which the composition of the liquid is equal to the composition of the feed. This is a limiting case. In the working-column with finite number of sections, and reflux greater than minimum, the feed should be introduced into that section in which the composition of the liquid is slightly less than that of the feed. The exact point is selected as follows:

Let the composition of the liquid in the column at the point where the feed is introduced be designated as C_{LX}. When the feed and the liquid flowing down the column are mixed the composition of the resultant liquid is $C_{LM} = \frac{L_{M+1} + C_{LX} + L_F C_{LF}}{L_{M+1} + L_F}$. The number of sections in the column is equal numerically to the area under the $\frac{1}{\Delta C_{LB}} \sim C_{LB}$ curve from C_{LS} to C_{LX}, plus the area under the $\frac{1}{\Delta C_{LN}} \sim C_{LN}$ from C_{LM} to C_{LP}. (See Figure 19.) C_{LX} must be so selected as to make the sum of these areas a minimum. The composition C_{LX} in most instances is so close to C_{LF} that a negligible error is involved in introducing the feed into that section of the column in which the composition of feed and liquid in the column are equal. If it should appear, from the curves showing the reciprocal of the rate of enrichment (Figure 19) above and below the feed-section, that an important error will be introduced by taking $C_{LF} = C_{LX}$, the value of C_{LX} can be determined graphically in accordance with the principles given above.

The reader will note that the designated location of the feed-section is not in agreement with that indicated by W. K. Lewis [37] and collaborator C. S. Robinson,[38] who state that the feed should enter column "on that plate at which the enrichment curves for tom and top of the column intersect as otherwise effi-

Eng. Chem., 14 (1922), 496-7.
...ments of Fractional Distillation," pp. 55-61. Also *J. Ind. Eng. Chem.*, 14 (1922), 481.

ciency of utilization of the plates is sacrificed."[39] From this it is evident that Lewis postulates that the feed should enter the column at a point where the rates of change of composition of liquid before and after the addition of the feed are equal. The reasons for my disagreement with this postulation are apparent from the above discussion.

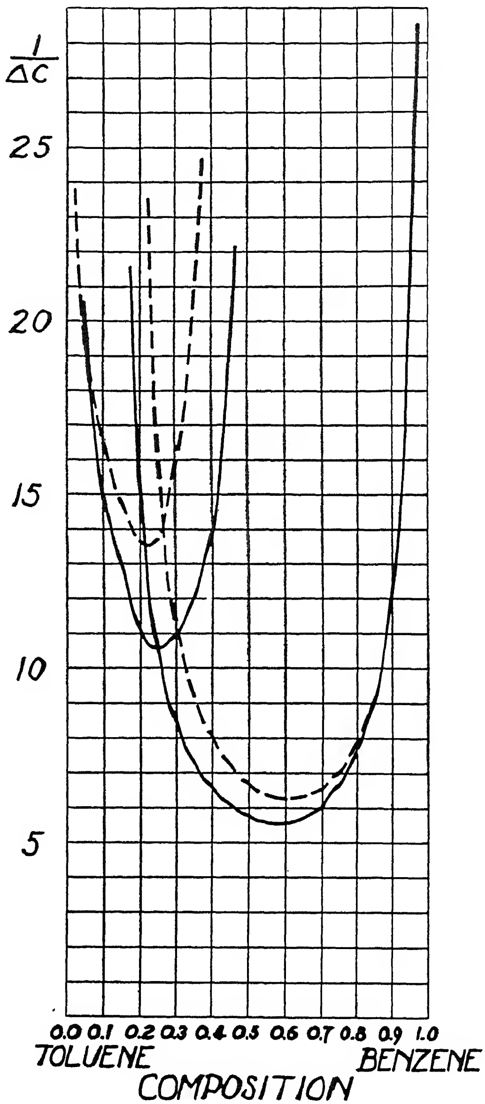


FIG. 19. $\frac{1}{\Delta C} \sim C_L$ Curve.

Temperature of the Feed.

The temperature of the feed should be the same as that of the liquid in the mixing-section. In discussing the perfect column the temperature of the feed and the liquid in the mixing-section was considered the same. This condition is not ordinarily fulfilled in the working column, and as a consequence the still is called upon to furnish the heat required to raise the feed to the temperature of the liquid on the feed-plate. Since this heat is supplied by condensation of vapor the weights of liquid and vapor flowing in the column below the mixing-section will be somewhat larger than those calculated by use of equations that do not take heating into account. This does not mean that this factor should be neglected.

Illustrative Problem—Continuous Distillation.

A solution containing 30 per cent benzene and 70 per cent toluene by weight is to be distilled in a continuous column to make a product

[39] Lewis, *loc. cit.*

containing 95 per cent benzene and 5 per cent toluene and a still-residue containing 10 per cent benzene and 90 per cent toluene. What weight of liquid must be fed to the column to make unit weight of product? What minimum weight of liquid would needs be refluxed if the column used in the separation were the ideal column? How many perfect sections must be in the column above and below the feed-section when the reflux-ratio is 4.0? When the reflux-ratio is 6.0? Where should the feed be introduced? Pressure is assumed constant throughout the apparatus and equal to 750 mm. of mercury.

Solution of the Problem.

1. Weight of Feed.

Use equation (26),

$$L_F = \frac{L_P(C_{LP} - C_{LS})}{C_{LF} - C_{LS}} = \frac{1.0\ (.95 - .10)}{.30 - .10} = 4.25$$

2. Minimum Reflux for Ideal Column.

In order to select a suitable reflux-ratio for the working column it is desirable to know the minimum reflux for the ideal column. Equation (40) can be used in this instance since benzene and toluene form concentrated perfect solutions.

$$L'_R \underset{\text{approx.}}{=} \frac{V'_S[C_{VS}(M_A - M_B) + M_B]}{C_{LP}(M_A - M_B) + M_B} - L_P$$

$$\underset{\text{approx.}}{=} \frac{V'_S\ [0.203(92 - 78) + 78]}{0.95(92 - 78) + 78} - 1.0$$

$$\underset{\text{approx.}}{=} 0.886\ V'_S - 1.0$$

The value of V'_S is found from equation (33),

$$V'_S \underset{\text{approx.}}{=} \frac{[C_{VF}(M_A - M_B) + M_B] \cdot L_P(C_{LP} - C_{LF})}{[C_{VS}(M_A - M_B) + M_B]\ \ (C_{VF} - C_{LF})}$$

$$\underset{\text{approx.}}{=} \frac{[0.508(92 - 78) + 78]\ \ 1.0(0.95 - 0.30)}{[0.203(92 - 78) + 78]\ \ (0.508 - 0.300)}$$

$$\underset{\text{approx.}}{=} 3.28$$

Hence,

$$L'_R = (0.886 \times 3.28) - 1.0 = 1.91$$

Since the minimum reflux in the ideal column is 2.91 the reflux-ratio used in operating the working column must be larger than this. It will be noted that in stating the problem reflux-ratios of 4.0 and 6.0 were chosen. This choice was based on a previous calculation of the value of L'_R.

3. Calculation of Number of Perfect Sections in the Column.

Reflux-ratio = 4.0.

The first step in calculating the number of sections in a continuous column is the construction of the $\frac{1}{\Delta C_L} \sim C_L$ curves for the portions of the column above and below the feed-section. The method of constructing the $\frac{1}{\Delta C_{LN}} \sim C_{LN}$ curve, that is, the curve for the portion of the column above the feed-section, is identical with that used in constructing the analagous curve for the column of the batch-still. Values of V_N for the chosen values of C_{LN} are calculated by means of equation (47), and corresponding values of ΔC_{LN} by means of equation (45).

The construction of the $\frac{1}{\Delta C_{LB}} \sim C_{LB}$ curve is based on values of ΔC_{LB} calculated by means of equation (54). The value of V_B in this equation may be found from equation (40). From the derivation of equation (40) it is evident that V_B and C_{VB} may be substituted for V_S and C_{VS}.

The results of all calculations are shown in Table XXIV.

TABLE XXIV

VALUES OF QUANTITIES USED IN SOLUTION OF CONTINUOUS DISTILLATION PROBLEM. $L_R = 4.0$

C_{LN} or C_{LB}	C_{VN} or C_{VB}	V_N or V_B	ΔC_{LN}	$\frac{1}{\Delta C_{LN}}$	ΔC_{LB}	$\frac{1}{\Delta C_{LB}}$
0.95	0.980	4.98	0.0376	26.6	......	....
0.90	0.960	4.99	0.0626	16.0	......	....
0.80	0.913	5.03	0.1038	9.6	......	....
0.70	0.857	5.07	0.1340	7.5	......	....
0.60	0.792	5.13	0.1538	6.5	......	....
0.50	0.714	5.19	0.1574	6.4	......	....
0.40	0.620	5.27	0.1424	7.0	0.0217	46.1
0.35	0.567	5.32	......	....	0.0407	24.6
0.30	0.508	5.36	0.1080	9.3	0.0541	18.5
0.25	0.445	5.42	0.0806	12.4	0.0660	15.2
0.20	0.375	5.49	0.0467	21.4	0.0730	13.7
0.15	0.293	5.57	......	....	0.0721	13.9
0.10	0.203	5.65	......	....	0.0655	15.3
0.05	0.112	5.75	......	....	0.0576	17.4
0.00	0.000	5.86	......	....	0.0357	28.0

The curves constructed from the data in Table XXIV are the dotted-line curves shown in Figure 19.

Assuming $C_{LX} = C_{LF} = 0.3$ the area under the $\frac{1}{\Delta C_{LN}} \sim C_{LN}$ curve between $C_{LN} = 0.95$ and $C_{LN} = 0.30$ is 5.34, and the area under the $\frac{1}{\Delta C_{LB}} \sim C_{LB}$ curve from $C_{LB} = 0.30$ to $C_{LB} = 0.10$ is 2.89. The total area is the sum of these areas or 8.23. The perfect

sections of the column apparatus are thus as follows: The still is one perfect section. The number of perfect sections in the column is 7.23 of which 5.34 are above the feed section. The number of plates or the length of packed-column in any working apparatus should be distributed accordingly.

4. Calculation of Number of Perfect Sections in the Column.

Reflux-ratio = 6.0.

The procedures for calculating the quantities and plotting the curves in this case are entirely analogous to those indicated under (3). The calculated quantities are given in Table XXV and the curves are the solid-line curves of Figure 19. The area under the $\frac{1}{\Delta C_{LN}} \sim C_{LN}$ curve between $C_{LN} = 0.95$ and $C_{LN} = 0.30$ is 4.86. The area under the $\frac{1}{\Delta C_{LB}} \sim C_{LB}$ curve between $C_{LB} = 0.30$ and $C_{LB} = 0.10$ is 2.37. The total area is the sum of these, or 7.23. The number of perfect sections in the column is 6.23 of which 4.86 are above the feed-section.

5. Location of Feed-Section.

The location of the feed-section has been discussed, but it is of interest to note the difference in number of perfect sections required when the feed is introduced where $C_{LX} = C_{LF}$ or at the composition represented by the point where the $\frac{1}{\Delta C_{LN}} \sim C_{LN}$ and $\frac{1}{\Delta C_{LB}} \sim C_{LB}$ curves intersect. The corresponding areas or number of perfect sections required in the two cases are shown in Table XXVI. Inspection of the last column in the table illustrates the point that introduction of the feed at the one point or at the other does not greatly influence the number of perfect sections required. In view of this fact and since introduction of the feed at either of these points is to be regarded as a limiting case, there is little object in making an elaborate effort to locate the exact point at which the feed should enter the column.

Fractionating Apparatus Other Than the Column.

In many industries other than the petroleum industry, in which fractionation is an important plant procedure, column apparatus has been used almost to the exclusion of other types of equipment for producing fractionation. Peculiarly enough, the petroleum industry has taken but slight advantage of the usefulness of column apparatus, but has used dephlegmating equipment almost exclusively. The importance of these apparatus in petroleum technology leads me to include a brief discussion of underlying principles, and a comparison of their effectiveness and efficiency with that of column apparatus. I do not wish to imply that column apparatus should be used in every instance

TABLE XXV

VALUES OF QUANTITIES USED IN SOLUTION OF CONTINUOUS DISTILLATION PROBLEM. $L_R = 6.0$

C_{LN} or C_{LB}	C_{VN} or C_{VB}	V_N or V_B	ΔC_{LN}	$\frac{1}{\Delta C_{LN}}$	ΔC_{LB}	$\frac{1}{\Delta C_{LB}}$
0.00	0.000	8.20	......	....	0.0284	36.2
0.03	0.070	8.11	......	....	0.0486	20.6
0.05	0.112	8.05	......	....	0.0586	17.1
0.10	0.203	7.91	......	....	0.0732	13.7
0.12	0.240	7.87	0.0167	60.0	......	....
0.15	0.293	7.80	0.0464	21.6	......	....
0.17	0.327	7.84	......	....	0.0905	11.1
0.20	0.375	7.70	0.089	11.2	0.0935	10.7
0.25	0.445	7.60	0.118	8.5	0.0914	11.0
0.30	0.508	7.53	0.140	7.1	0.0850	11.8
0.40	0.620	7.37	0.168	5.0	0.0606	16.5
0.45	0.668	7.31	......	....	0.0431	23.2
0.50	0.714	7.26	0.176	5.7	0.0237	42.1
0.60	0.792	7.18	0.166	6.1	......	....
0.70	0.857	7.10	0.142	7.1	......	....
0.80	0.913	7.04	0.107	9.4	......	....
0.90	0.960	7.02	0.0616	16.3	......	....
0.95	0.980	7.01	0.0350	28.6	......	....

TABLE XXVI

DATA BEARING ON LOCATION OF FEED-SECTION

Reflux Ratio L_R	Area or Number of Perfect Sections						Difference of Totals
	$C_{LX} = C_{LF}$			$C_{LX} = C_L$ at Intersection			
	Above Feed	Below Feed	Total	Above Feed	Below Feed	Total	
4.0	5.34	2.89	8.23	5.77	2.60	8.37	0.14
6.0	4.86	2.37	7.23	5.32	2.14	7.46	0.23

where dephlegmating equipment is now used, although in many instances a change to column apparatus would prove profitable.

In the following paragraphs I shall consider the simple and the differential dephlegmators or fractionating condensers.

The word "dephlegmator" is loosely used. The refinery engineer usually refers to some type of fractionating condenser when he uses this term. Webster's International Dictionary defines "dephlegmator" as "the part of a distilling apparatus in which a partial separation of the vapors of water and alcohol is effected as by means of cold metallic diaphragms." I can hardly concede that this limited definition is of any special value. As descriptive of laboratory apparatus, particularly in British writings, the term indicates an apparatus in which "washing"

or intimate contacting of liquid and vapor occur. I prefer the word "column," the phrase "column-still," or, if referring to laboratory apparatus, the phrase "still-head," to designate this type of apparatus. The word "reflux" or "partial-condenser" is applicable to the condensing apparatus that returns a part of the vapor (as liquid) to the column. The terms "dephlegmator," "fractionating-condenser," "fractionating-reflux," or "regulated-temperature still-head," modified when necessary for clearness by the adjective "simple" or "differential," should be used to describe the fractionating apparatus intended to produce separation by fractional condensation.

The fractionating-condenser should be distinguished from the reflux or partial-condenser used in conjunction with a fractionating-column. The reflux is not intended to better the results of the separation obtained in the column, but to condense a definite part by weight of the vapors leaving the column. The liquid so formed is returned to the column. The fractionating-condensers discussed below are intended to produce, by a process of fractional condensation, a vapor richer in the volatil component than the vapor entering the apparatus.

Two limiting types of dephlegmators should be distinguished, and will be discussed in the following paragraphs:

1. The simple dephlegmator.
2. The differential dephlegmator.

Nomenclature.

The following symbols will be used in discussing the results obtainable by the use of both types of apparatus.

C_{LS} = composition of liquid in still.

V_S = weight of vapor formed in the still and entering the fractionating system.

C_{VS} = composition of vapor leaving still.

V_D = weight of vapor leaving the dephlegmator.

$C_{VD} = C_{LP}$ = the composition of the vapor leaving the dephlegmator.

C_{LD} = composition of the liquid in equilibrium with vapor of composition C_{VD}.

L_D = weight of liquid formed by condensation of vapor during separation of weight V_D of vapor of composition C_{VD}.

The Simple Dephlegmator.

The perfect simple dephlegmator is really a combination of a perfect column-section and a reflux operated as one apparatus at constant temperature. Figure 20 shows the relationship between temperature and composition of the phases of a binary solution such as benzene-toluene.

A weight of vapor V_S, of composition C_{VS}, enters the apparatus at temperature t_1. Upon cooling dt below t_1, an infinitesimal amount of liquid of composition $C_{LS} + dC_L$ is formed. If the temperature

of the dephlegmator were maintained at t_2 a weight of liquid L_D of composition C_{LD} would be formed, and a weight of vapor V_D of composition C_{VD} would pass as product to the final condenser. Were the temperature maintained at t_3 all of the vapor would be condensed to form a liquid of composition $C'_{LD} = C_{VS}$, that is, the composition of the vapor entering the dephlegmator from the still. Thus, the limit of enrich-

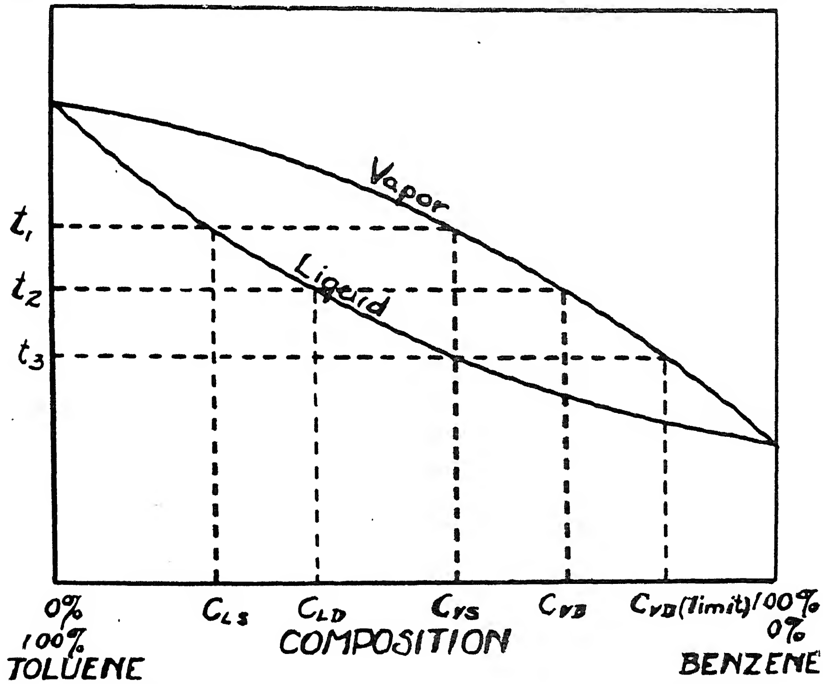


FIG. 20.—Temperature ~ Phase-Composition Diagram.

ment, $C_{VD\,(limit)}$, of a binary vapor is the composition of the vapor in equilibrium with a liquid of composition equal to C_{VS}, and the weight of the enriched vapor at this limit is zero. At temperatures between t_3 and t_1 enriched vapors can be formed. The weight of vapor that results when the dephlegmator is operated at any temperature between t_3 and t_1 may be calculated as follows: Equating weights of vapors and liquid entering and leaving the dephlegmator,

$$V_S = L_D + V_D \tag{55}$$

Hence,

$$V_S C_{VS} = L_D C_{LD} + V_D C_{VD} \tag{56}$$

Combining (55) and (56) to eliminate L_D,

$$V_S = \frac{V_D(C_{VD} - C_{LD})}{C_{VS} - C_{LD}} \tag{57}$$

Since C_{VS} is known, and for any temperature t_2 values of C_{LD} and C_{VD} can be read from the curves of Figure 20, the weight of vapor V_S, necessarily entering the dephlegmator to form a weight of product V_D, can be calculated.

The Differential Dephlegmator.

The ideal differential condensation process consists in the establishment of a succession of instantaneous equilibria between the vapor and the liquid formed from the vapor. The condensate is immediately and completely removed. Further condensation of the vapor forms successive differential quantities of liquid, with consequent enrichment of the vapor in the volatil component. The limit of the process is determined by the temperature at which the dephlegmator is operated.

Assume that a weight of vapor V_S of composition C_{VS} enters the dephlegmator. In the first instant a differential quantity of vapor is condensed. As a result of this the composition of the vapor changes from $C_{VS} = \frac{V_S C_{VS}}{V_S}$ to

$$C_{VS} + dC_V = \frac{V\ C_{VS} - dV \cdot C_L}{V - dV} \tag{58}$$

That is, the composition of the vapor after the differential change is equal to the weight of volatil component in the new vapor divided by the weight of the new vapor.

Rearranging the equation and discarding differentials of the second order

$$\frac{dV}{V} = \frac{dC_V}{C_V - C_L} \tag{59}$$

Integrating, between limits corresponding to the change occurring in the dephlegmator, that is, V_S and V_D for weights of vapor, and C_{VS} and C_{VD} for compositions of vapor,

$$\log_e \frac{V_S}{V_D} = \int_{C_{VS}}^{C_{VD}} \frac{dC_V}{C_V - C_L} \tag{60}$$

The right hand member of equation (60) can be evaluated if the equation of the curve showing the relationship between equilibrium values of C_V and C_L is known. In general, this question will not be known and the integral must be evaluated graphically. To do this draw a curve, each point of which represents a composition as abscissa and a value of $\frac{1}{C_V - C_L}$ as ordinate. Figure 21 shows this curve for the system benzene-toluene.

To evaluate the quantity $\int_{C_{VS}}^{C_{VD}} \frac{dC_V}{C_V - C_L}$ in equation (60) find the area bounded by the curve, the ordinates C_{VS} and C_{VD}, and the composition-axis. Equation (60) may thus be solved for the weight of vapor V_S necessarily formed in order to separate a weight of product V_D.

Comparison of Efficiency of Fractionation of the Simple and Differential Dephlegmators, and the Column.

The efficiencies of separation by these apparatus should be compared by calculating the heat required to produce unit weight of a

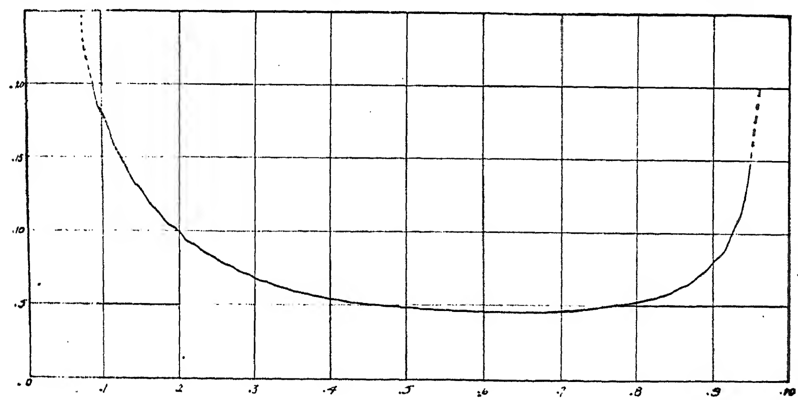


FIG. 21. $\frac{1}{C_V - C_L} \sim C_V$ Curve.

distillate of a chosen composition. However, data regarding specific heats of the vapors and liquids, and latent heats of vaporization, are very limited in number. Hence, the efficiencies will be compared on the basis of the weight of liquid necessarily evaporated to produce unit quantity of distillate of the chosen composition.

The solution considered will be benzene-toluene containing equal proportions of the components by weight. The vapor in equilibrium with this solution is of composition 0.716. Three cases will be considered,

1. Change in composition of vapor from 0.716 to 0.816.
2. Change in composition of vapor from 0.716 to 0.950.
3. Change in composition of vapor from 0.716 to 1.000.

The minimum vaporizations required in each of these three cases were calculated for the simple dephlegmator, the differential dephleg-

mator, and the ideal column by use of equations (57), (60), and (11), respectively. The results of these calculations are presented in Table XXVII.

TABLE XXVII

MINIMUM VAPORIZATION REQUIRED TO SEPARATE UNIT WEIGHT OF PRODUCT IN SIMPLE AND DIFFERENTIAL DEPHLEGMATORS AND IN THE COLUMN

Change in Composition of Vapor		Weight of Vapor Necessarily Formed in the Still in Order to Separate Unit Weight of Product		
From	To	Perfect Simple Dephlegmator	Perfect Differential Dephlegmator	Ideal Column
0.716	0.816	2.22	1.648	1.46
0.716	0.950	Separation Impossible	4.792	2.08
0.716	1.000	Separation Impossible	A zero quantity of product can be formed	2.32

The relative efficiencies of the three processes can now be compared. If the efficiency of the ideal column is taken as 100 per cent, the efficiencies of the simple and differential dephlegmators are 65.7 per cent and 88.7 per cent respectively in case (1), and 0 per cent and 43.5 per cent in case (2). In case (3) the separation can only be made by the column.

The foregoing data illustrate the greater efficiency of fractional distillation as compared to fractional condensation of either simple or differential type. Also the advantage of differential dephlegmation over simple dephlegmation is clearly shown.

The general proposition that fractional distillation is always more efficient than differential dephlegmation, and that differential dephlegmation is always more efficient than simple dephlegmation, is capable of mathematical proof.

Simple dephlegmation is easily realized in practice. The essentials of the process are constant temperature and intimate contact of liquid and vapor.

Differential dephlegmation is not so easily accomplished in practice, but it is entirely possible to approximate to this process by the use of an apparatus of the type shown in Figure 74 of Chapter VII.

The use of a column, or of the fractionator shown in Figure 76 in Chapter VII, is far more satisfactory than that of dephlegmators for most purposes.

Efficiency versus Effectiveness in Fractionation.

In view of the foregoing discussion of efficiencies it is desirable clearly to distinguish between the meaning of the phrases "efficiency" and "effectiveness" of fractionation. These or other similar phrases

are used very loosely and cause confusion. The phrase "effectiveness of fractionation" refers to the degree of the separation of one substance from a solution. The apparatus producing this result may be *effective* in its operation but not necessarily *efficient*. The time required is an important factor, for slow vaporization increases the "effectiveness" of the apparatus, but invariably lowers the thermal "efficiency" of the process.

The efficiency of fractionation, or more exactly, the thermal efficiency of fractionation, is the ratio of the heat required by any fractionating system to that required by the ideal system of the same type to accomplish a given separation.

Steam Distillation.

The use of steam in the distillation of petroleum oils is of great importance, yet the principles of steam distillation are often imperfectly understood. Steam does not "throw an oil over" in the sense of the literal interpretation of these words.

For purpose of illustration, consider that a hydrocarbon substance is being distilled with *wet* steam. The hydrocarbon and water are insoluble each in the other. In order that vapor may continuously exit from the distillation system, the total vapor-pressure must equal atmospheric pressure, or

$$P_{\text{atmosphere}} = P_{\text{steam}} + P_{\text{hydrocarbon}}$$

$$P_A = P_s + P_h$$

P_s and P_h are the partial pressure of water and the hydrocarbon at the particular temperature. If distillation is to take place the temperature must be raised until the sum of P_s and P_h equals the total pressure P_A. If the vapor-pressure curves of the non-miscible component substances are known the temperature at which the mixed vapor will form and exit from the system can be calculated, or conversely, the composition of the mixed vapor can be calculated if the vapor-pressure curves and the temperature are known. These statements are based on the postulate that the system is in equilibrium. Under these conditions the phase rule indicates that the system is univariant:

$$F = C + 2 - P$$

The number of components is two, the phases are three (water, hydrocarbon, and vapor), and the degrees of freedom $F = 2 + 2 - 3 = 1$. One choice of conditions can be made, and since it is desired to form vapor continuously this single choice is used when the pressure is necessarily selected as equal to that of the atmosphere. Temperature and phase-compositions are therefore defined.

The Use of Superheated Steam.

The writer has more than once been asked whether superheated steam should be used in steam distillation. Assume that the hydro-

carbon is confined in an ideal apparatus of the type shown in Figure 22. The liquid hydrocarbon is heated to a temperature such that its vapor-pressure is equal to P_A, the pressure of the atmosphere. If the temperature is lowered the piston will move downward and the vapor phase will disappear since at the lower temperature the vapor-pressure of the liquid is less than P_A. If superheated steam is introduced beneath the piston, the total pressure on the under side of the piston equals $P_h + P_s$. If the concentration (i.e., pressure) of superheated steam is increased, the sum of these pressures will become equal P_A and the piston will rise as the volume of mixed vapor increases. Vapor of the liquid is forming, but at a temperature less than the boiling point of the liquid at the particular pressure. The lower the temperature of the liquid, the greater the quantity of superheated steam required. At the boiling point of the liquid a zero quantity of steam is required. The maximum quantity of steam is used when the temperature has been lowered to such a point that the liquid phase water appears. At this point, as has already been shown, the system, at constant pressure, is invariant. Lowering the temperature would result in the disappearance of the vapor phase and distillation would stop.

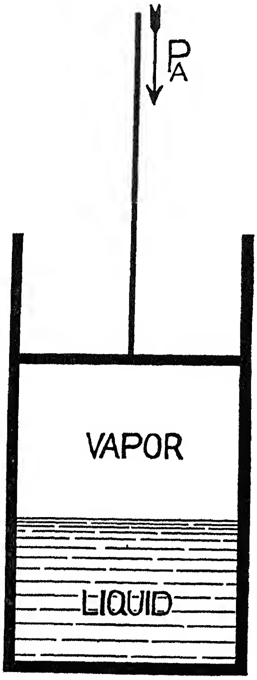


FIG. 22.—Ideal Cylinder and Piston.

The object of steam distillation is to distill at a lowered temperature. The maximum lowering is obtained when wet or saturated steam is used, but distillation may be conducted at any temperature between this temperature and the boiling point of the hydrocarbon if superheated steam is used.

In practice the steam available is frequently very wet, and it may be economical to superheat it to a moderate degree if waste heat can be so utilized.

A further factor that may modify calculations of steam requirements is the difficulty in obtaining equilibrium conditions. If steam is merely blown through oil in a still equilibrium will most certainly not be obtained. This suggests at once that the steam distillation of petroleum oils and distillates should always be conducted in column apparatus, for as I have indicated this apparatus is designed to cause intimacy of vapor and liquid phases and an approach to equilibrium conditions.

The Steam Distillation of Hydrocarbon Mixtures.

The foregoing reasoning may be applied equally well to systems of several components. Gasoline is composed of a number of hydro-

carbons. For the sake of definite expression assume the number of components to be 10. In accordance with the phase rule, the number of degrees of freedom of the system gasoline-water is

$$F = 11 + 2 - 3 = 10$$

The independent variables are the pressure, the temperature, and the concentration of nine hydrocarbon components of the liquid mixture. If the concentration of nine of the components is fixed the concentration of the tenth component and the composition of the vapor in equilibrium are necessarily fixed. Nine of the ten degrees of freedom of the system are thus lost when we have selected the particular ten-component liquid phase. One degree of freedom still remains. If pressure is now fixed as necessarily equal to that of the atmosphere, temperature and composition of the vapor phase are fixed and the system is completely defined.

It is simpler to think of the gasoline as one component than as a mixture of many components, and at any instant this may be done. But as time passes, the composition of the gasoline changes, that is, the concentration of the components varies, and the temperature of the system and composition of the vapor phase change accordingly.

Chapter V.

Fluid Flow and Heat Transfer.

The production of the lighter distillates from petroleum involves the use of many kinds of heating, condensing, and cooling equipment. The design of these apparatus and the interconnecting piping requires a knowledge of the laws of flow of gases and liquids and of the principles of heat transfer. It is quite without the scope of this book to discuss fluid flow and heat transfer in the greatest detail. However, the material that follows will be found helpful, and when taken together with the material in Chapter IV on fractional distillation, offers a basis for the design of most refinery equipment.

The Flow of Fluids in Pipes or Tubes.

Until recently the calculation of the flow of gases and liquids in pipes has been approached with some misgivings by the engineer. Data were scattered and none too concordant. A few special fields such as the flow of water, of air, and of viscous liquids in small tubes had been investigated with care, but no correlated treatment of the whole subject of fluid flow was at hand. To Messrs. Stanton, Pannell, Higgins,[1] and other investigators working in the National Physical Laboratory, belongs the credit for correlating the work of previous investigators, and of adding thereto many new as well as confirmatory data. Somewhat more accessible to engineers in this country are the later papers of A. C. Preston,[2] and of R. E. Wilson, W, H. McAdams, and M. Seltzer.[3]

Preston, perhaps too modestly, states that his own contribution is "chiefly to correlate and adapt the work of others so as to put the whole in familiar and convenient form for use in general engineering design." He, however, carried out a fairly extensive series of experiments on the flow of oil in wrought iron pipes at the University of Colorado.

Wilson, McAdams and Seltzer have likewise reviewed the literature and have gathered together much of the useful information therein. This they have supplemented by experimental work on the flow of oils of several densities and viscosities.

[1] Collected Researches, National Physical Laboratory. Teddington, England, 11 (1914), 13 (1916).
[2] *Chem. Met. Eng.*, 23 (1920), 607-13, 685-89.
[3] *J. Ind. Eng. Chem.*, 14 (1922), 105-119, 462.

These papers as well as those included in the appended bibliography are commended to the reader. They have been drawn upon freely in writing the paragraphs that follow.

The similarity in motion of fluids of widely differing densities and viscosities was predicted by Stokes[4] in 1850, by Helmholtz[5] in 1893, by Osborne Reynolds[6] in 1882, and by Lord Rayleigh[7] in 1899 and 1909. Reynolds conducted experiments in which he introduced coloring substances into water flowing through glass tubes, and showed that at low velocities the flow was stream-like or lamellar in character, and sinuous or turbulent at higher velocities. The change from lamellar to turbulent flow took place suddenly at a velocity designated as the "critical velocity," the value of which is inversely proportional to the diameter of the tube and directly proportional to the kinematic viscosity,[8] that is

$V_c = \text{constant}\left(\frac{z}{Ds}\right)$, or the constant, which may be designated as "k," is:[9]

$$k = \frac{V_c Ds}{Z}$$

The flow of fluids is governed by two types of factors, one that may be designated as inherent, and another that includes pipe size, roughness, and other factors that are variable at will. The inherent factors are viscosity and density. The ordinary theory of hydraulics neglects the inherent factors such as change of density and viscosity with temperature, and for this reason is not a general exposition of the subject of fluid flow. The development of a general theory of fluid flow must take into account all factors.

The findings of Reynolds and other scientists, though often buried in little read journals or transactions, and clothed in a formidable mathematical garb, have come to be appreciated at least in a general

[4] "Mathematical and Physical Papers," Vol. III, 17.

[5] "Wissenshaftliche Abhandlungen," Vol. I, 158.

[6] *Phil. Trans. Roy. Soc.*, London, 1883, 935.

[7] "Advisory Comm. for Aeronautics Rep.," 1909-10, 38.

[8] Kinematic viscosity $= \frac{\text{absolute viscosity}}{\text{density}} = \frac{z}{s}$

[9] The following nomenclature, which is the same as that of Wilson, *et al.*, will be used, and all formulas, regardless of source, will be translated into these terms. The units, it will be noted, are those of engineering practice rather than of the laboratory.

f = friction factor (Fanning)
l = length of pipe or tube in feet
v = average linear velocity in the line of the pipe in feet/second
z = viscosity in centipoises
p = pressure drop in pounds/square inch
s = specific gravity $\left(\frac{t^\circ}{4^\circ \text{C.}}\right)$ of the fluid
D = inside diameter of the pipe in inches
Q = flow of liquid in gallons/minute.

way. Liquids move through pipes in stream-line flow up to the range of critical velocities, and above this in an eddying and turbulent manner. To be accurate one must refer to a range of critical velocities rather than to designate a particular velocity as the critical velocity, for the change from unidirectional flow to turbulent flow is conditioned by several factors that are capable of variation, such as roughness of the pipe, vibration, and presence of fittings.

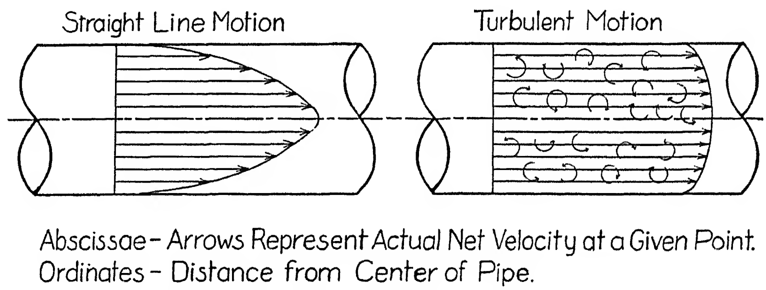


FIG. 23.—Graphical Representation of Viscous and Turbulent Flow in Pipes.

The two types of flow are depicted graphically in Figure 23.[10] The velocity of the liquid on the wall of the pipe in straight line or viscous flow is 0. The mean velocity is one-half the velocity of the liquid flowing along the axis of the pipe. These facts have been predicted on purely mathematical grounds, and have been verified experimentally. When the flow is of the straight-line or viscous type the volume of fluid flowing in time "t" is given by Poiseuille's [11] law.

$$V = \frac{\pi p r^4 t}{8 z l}$$

This may be transformed to give the pressure drop in a pipe of length "l" and diameter D in terms of the given nomenclature.

$$p = \frac{0.000668 \ z \ l \ v}{D^2}$$

The formula for the pressure drop when the fluid flow is turbulent is that of Fanning, which, expressed in our nomenclature, is

$$p = \frac{0.323 \ f \ l \ s \ v^2}{D}$$

in which "f" is a friction factor the value of which is a function of the density, viscosity, mean velocity of the fluid, and of the size and

[10] Wilson, McAdams, and Seltzer.

[11] Jean-Louis-Marie Poiseuille, French physician, anatomist, and physiologist. His interest in the flow of blood in the veins and arteries led to his researches on the flow of liquids in capillaries, the results of which were published in 1844.

character of the pipe. In order to use Fanning's formula it is necessary to know the value of the variable factor "f". Many attempts have been made to formulate general equations in which "v" and "D" have been raised to powers ranging from 1.6 to 1.9 for "v," and 1.4 to 1.1 for D. Equations of this nature may be used in a limited way only.

It was predicted by Stokes[12] and by the several others mentioned above under the discussion of Reynolds "critical-velocity," that "f" is not a function of v, D, s and z as independent variables, but only of the non-dimensional expression $\frac{Dvs}{z}$, i.e.,

$$\text{"f"} = \Phi\left(\frac{Dvs}{z}\right)$$

This happily allows of the formulation of a general expression that can be used for the calculation of pressure drop, whether the flow is viscous or turbulent. If Poiseuille's law and Fanning's equation are written side by side it can be seen[13] that if "f" $= 0.00207 \frac{z}{Dvs}$ then the two equations are identical.

If, in the graphic representation of experimental data, "f," in Fanning's equation is plotted as ordinate against the corresponding value of $\frac{Dvs}{z}$, a useful curve is obtained.

Obviously the values of "f" calculated from the expression $f = 0.00207 \frac{z}{Dvs}$ can be plotted against $\frac{Dvs}{z}$ on this same chart. If logarithmic paper is used the latter curve will be a straight line.

It is now possible to represent all experimental results and to make all calculations with Fanning's equation. When the value of "f" calculated from this equation falls on the straight line $f = 0.00207 \frac{z}{Dvs}$ it indicates that Poiseuille's law holds and that the flow is viscous or stream-line.

As long as the flow is of the viscous type it is independent of the nature of the pipe or tube. This is obvious, since the fluid layer nearest the tube wall moves with zero velocity.

If the flow is turbulent "f" is a function not only of $\frac{Dvs}{z}$, but of the nature of the pipe or tube, particularly as regards roughness. Hence, the curve expressing the relationship between log "f" and log

[12] *Math. and Phys. Papers,* III (1850), 17.

[13] Blasius, *Z. Ver. Deut. Ing.,* 56 (1912), 639:

$$p = 0.00668\frac{lvz}{D^2} \qquad \text{(Poiseuille)}$$

$$p = 0.323\frac{flsv^2}{D} \qquad \text{(Fanning)}$$

$\frac{Dvs}{z}$ for a smooth tube will be somewhat different from that for commercial mild-steel or cast iron pipe.

Figure 24 is a slight rearrangement of the graph of "f" $\sim \frac{Dvs}{z}$ as given by Wilson, McAdams, and Seltzer. They have carefully studied their own and the data assembled from the literature, and have given what they believe to be the best values of "f" for clean commercial wrought-iron, steel, or cast-iron pipes for diameters of 1-inch to 8-inches. The National Physical Laboratory data on "f" for smooth tubes are also plotted. The value of "f" for large pipes probably deviates toward the curve for smooth tubes, and that of "f" for very rough pipes is higher than that given for commercial steel and cast pipe.

Before discussing methods of calculation it is essential to consider the effect of fittings on flow. Data on this subject are none too plentiful.

Effect of Ells on Fluid Flow.

The frictional resistance of a fitting is most conveniently expressed in terms of the length of straight pipe that would offer the same resistance to flow. More commonly this equivalent length of straight pipe is expressed in terms of pipe diameters. The figure is therefore nearly the same for all pipe sizes. The usual allowance for an ell is a straight pipe length equal to 30 to 50 pipe-diameters. These figures are justified when calculating the flow of water. The use of the factor 50 is more than ample.

Wilson, McAdams and Seltzer have investigated the effect of ells on the flow of oils, and conclude that the value 30 pipe-diameters allowance per ell is about the right factor to use when the flow is turbulent. However, when the flow is viscous, the factor varies with $\frac{Dvs}{z}$, decreasing from about 30 to 2.5 diameters. The upper curves of Figure 24 are a graphical showing of these facts.

Method of Making Calculations.

Calculations of the flow of fluids in pipes involve six variables,—the diameter and length of the pipe, the specific gravity and viscosity of the fluid, the pressure drop, and the velocity of flow or the quantity discharged in a given time. Five of the six variables D, l, s, z, p, and v, must be known or assumed. A brief discussion of the methods for determining the values of each of these quantities is given herewith.

Diameter of the Pipe.

The nominal diameters used commercially in designating pipe sizes are not the same as the actual internal diameters. Table XXVIII [14]

[14] Wilson, McAdams, and Seltzer.

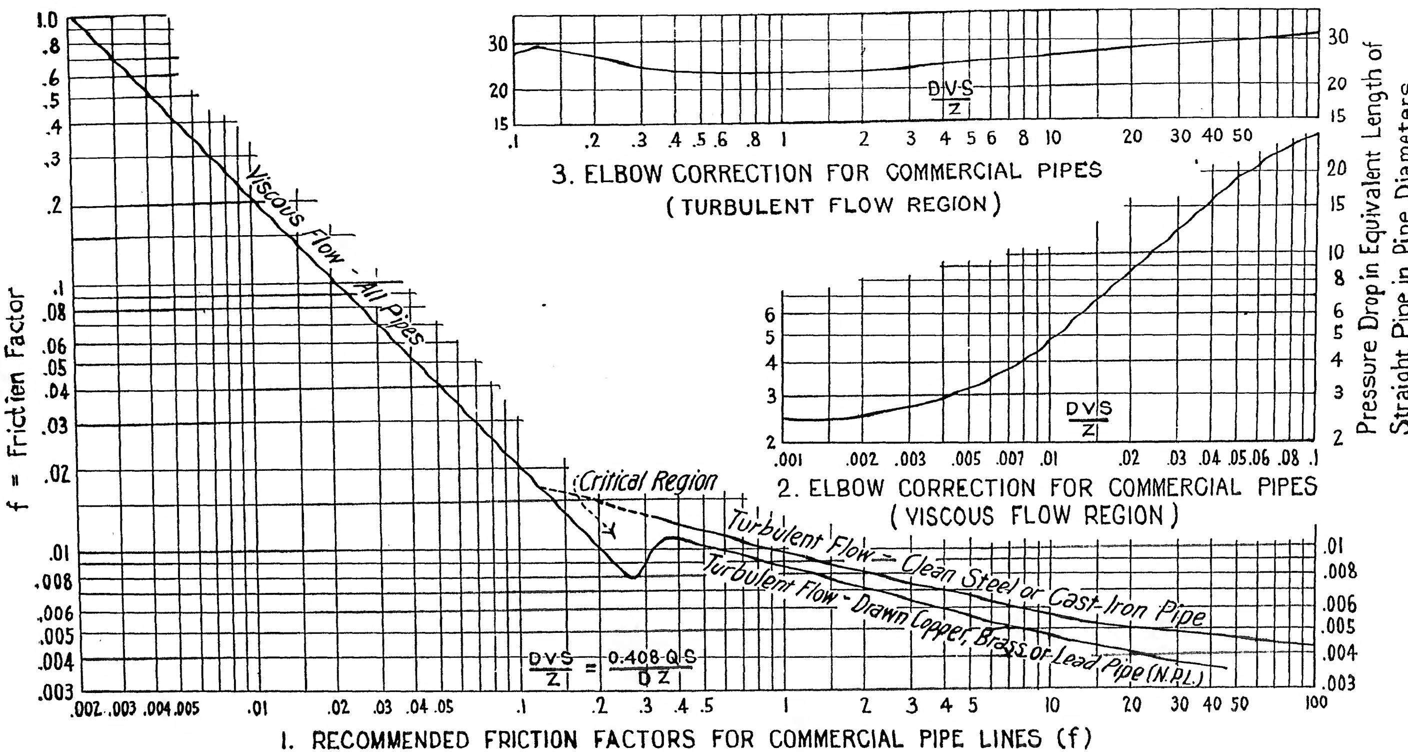


FIG. 24.—Friction Factor and Elbow Correction for Commercial Pipes.

gives the nominal diameter and the diameter functions for Standard iron and steel pipe. The actual dimensions of extra-heavy pipes and of tubes can be obtained from handbooks and tables published by manufacturers. Diameters should be expressed in inches.

TABLE XXVIII

DIAMETER FUNCTIONS OF STANDARD IRON AND STEEL PIPE

Nominal Diameter	Actual Inside Diameter—Inches	D^2	D^4	D^5	Actual Internal Cross-section Area
In.	D				Sq. in.
0.5	0.622	0.3869	0.1497	0.09310	0.3039
0.75	0.824	0.6790	0.4610	0.3799	0.5333
1.0	1.049	1.100	1.211	1.270	0.8639
1.5	1.610	2.592	6.719	10.82	2.036
2.0	2.067	4.272	18.25	37.73	3.356
2.5	2.469	6.096	37.16	91.75	4.786
3.0	3.068	9.413	88.60	271.8	7.392
4.0	4.026	16.21	262.7	1058.0	12.73
6.0	6.065	36.78	1353.0	8206.0	28.89
8.0	8.071	65.14	4243.0	34250.0	51.15
8.0	7.981	63.70	4057.0	32380.0	50.02
10.0	10.192	103.8	10790.0	109980.0	81.55
10.0	10.136	102.7	10560.0	106990.0	80.75
10.0	10.020	100.4	10080.0	101000.0	78.82
12.0	12.090	145.9	21370.0	258300.0	114.80
12.0	12.000	144.0	20736.0	248800.0	113.10
14.0	13.250	175.5	30750.0	407500.0	137.7
16.0	15.250	232.5	54200.0	825100.0	182.7
18.0	17.250	297.2	88500.0	1526000.0	224.0
20.0	19.250	370.5	137300.0	2640000.0	291.1
24.0	23.250	540.0	291900.0	6777000.0	424.5

Length of Pipe.

of the pipe should be expressed in feet. The correction be made by use of the curves in Figure 25.[15] For pipes liameters long the entrance and exit losses must be taken ~his is mentioned later.

Specific Gravity.

The specific gravity must be expressed as the ratio of the density of the fluid under working conditions to the density of water at 4° C. or 39.2° F. The density of water at 4.0° C. is a maximum and is

[15] Taken from Wilson, McAdams and Seltzer's article, Figure 11 on which plot they have assembled their own data, and those of
Balch, Univ. of Wis., *Bull. Eng. Ser.*, *7*, No. 3, 253, Paper No. 578.
Giesecke, Univ. of Texas, *Bull. 1759*, Oct. 20, 1917.
Daly, Schroder and Bain, *Cornell Civ. Eng.*, 20 (1911-12), 107.
Davis, Univ. of Wis., *Bull Eng. Ser.*, 6, No. 4, 115.

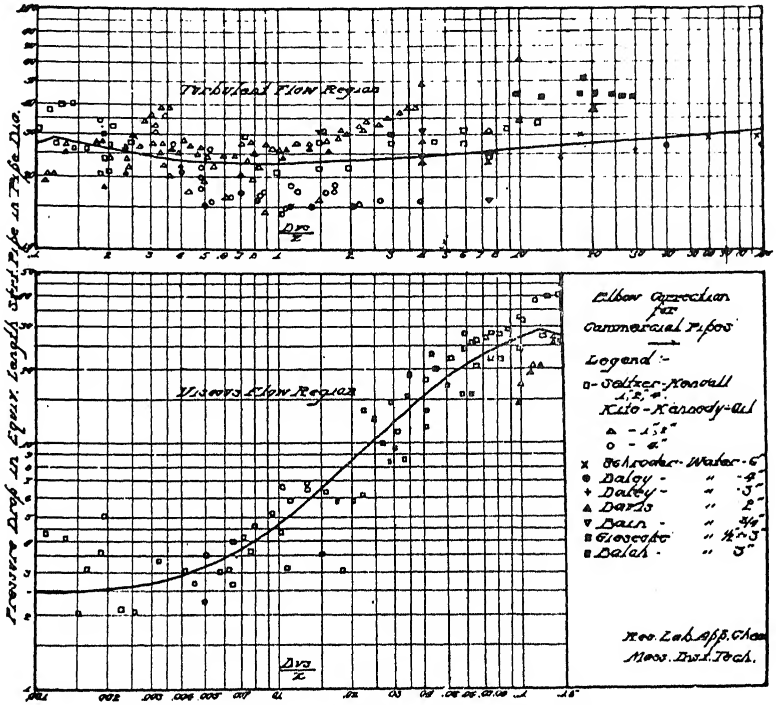


FIG. 25.—Elbow Correction for Commercial Pipes.

equal to 1.00000. Hence, the value of "s" to be used in calculations is the true density at working conditions. If the gravity is measured in Baumé degrees the conversion to specific gravity should be made by the proper modulus for the particular hydrometer. It is preferable to use a specific gravity balance, and avoid the Baumé conversion.

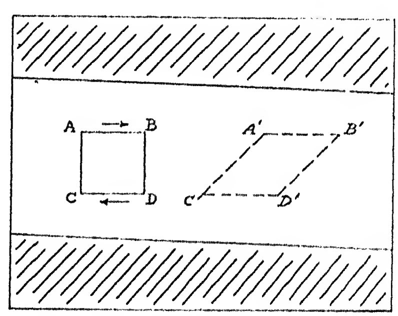


FIG. 26.—Shearing of a Fluid.

Viscosity.

The widespread use of commercial instruments in the measurement of viscosity is perhaps responsible for the fact that our physical conception of viscosity is often somewhat beclouded. A brief review of the subject of viscosity may therefore be in point.

Consider a cube of liquid ABCD in a stream of liquid that is flowing down a very gentle incline as shown in Figure 26. The liquid

above AB is exerting a force in the direction of the arrow A ⟶ B and that below the cube a resistance in the direction D ⟵ C. The result is a shearing stress that tends to distort the cube to the form A′B′C′D′. Extensive experimentation has shown that for any fluid the ratio of the shearing stress to the rate of shear is a constant. This is called the coefficient of viscosity for the fluid. Different fluids have different coefficients of viscosity.

Consider two parallel plates of area A, at a distance "d" apart, moving in a fluid in such a manner that the velocity of one with respect to the other is V. In time "t" one plate will move a distance Vt with respect to the other plate. The shear produced will be $\frac{Vt}{d}$. The rate of shear is $\frac{V}{d}$. If the force applied to the more rapidly moving plate is F, the shearing stress is $\frac{F}{A}$. Then, if a constant is designated as μ

$$\mu = \frac{F/A}{V/D}$$

or

$$F = \mu \cdot \frac{AV}{d}$$

If now A, V, and d are unity, $F = \mu$

The coefficient of viscosity (or the "viscosity") is thus seen to be equal to the tangential force on unit area of either of two horizontal planes at unit distance apart, one of which is fixed while the other moves with unit velocity, when the space between them is filled with fluid.

This definition shows at once that if viscosity is to be measured in any instrument the latter must be so arranged that the motion of the liquid planes is unidirectional. There must be no eddying or turbulence. The commonest method of evaluating μ is to measure the rate of flow of a fluid through a capillary tube, in which event the volume flowing in unit time is

$$V = \frac{p\pi r^4}{8\,l\mu} \qquad \text{(Poiseuille's law)}$$

The C.G.S. unit of viscosity is the poise, i.e., the force in dynes required to move a plane of one sq. cm. area, distant one centimeter from another plane of unit area, one centimeter in one second.

The unit used in the present discussion is the centipoise (1 poise = 100 centipoises).

Practically, it is convenient to use vertical rather than horizontal tubes for the measurement of viscosity. The force is the pressure due to gravity head. The resistance is a summation of all the resistances to fluid slip. If there is no increase in velocity during flow the

force can be equated to the fluid resistance. If the tube through which the liquid flows is larger than a fine capillary part of the force is expended in increasing the kinetic energy of the fluid. Correction must be made for this [15a] as well as for turbulence from "end effects."

The reason for the fact that the Saybolt Universal and the other commercial viscosimeters do not measure absolute viscosity directly is now apparent. When the original Saybolt instrument was designed it was intended [16] that the flow through it should be stream-line or viscous. The instrument as now made [16a] consists of a smooth vertical efflux tube, 1.225 cm. long, and 0.1765 cm. in diameter. Above the tube is a vertical cylinder 2.975 cm. in diameter and 9.7 cm. long. This is connected to the efflux tube by a converging section about 1.575 cm. long. The height from bottom of outlet tube to overflow rim is 12.6 cm. The upper chamber holds about 70 c.c., and is surrounded by a water bath so that the fluid may be held at a constant temperature. The Saybolt viscosity is the time in seconds required for the efflux of 60 c.c. of the liquid.

If the flow of the liquid were stream-line the time of efflux would be proportional to the kinematic viscosity (i.e., equal to $\frac{\text{viscosity}}{\text{density}}$ or $\frac{z}{s}$).

But the flow is somewhat turbulent so that the kinematic viscosity must be calculated by the relationship

$$\frac{z}{s} = 0.220\ t - \frac{180}{t}$$

where "t" is the Saybolt viscosity, or the time in seconds required for the efflux, z the viscosity in centipoises, and s the specific gravity. When the Saybolt viscosity is higher than 300 seconds the error in the assumption that the Saybolt viscosity is proportional to kinematic viscosity, that is,

$$\frac{z}{s} = 0.220\ t$$

is only 0.9 per cent. If the Saybolt viscosity is 1000 the error in this assumption is only 0.1 per cent.[17] The dimensions of Saybolt viscosimeters vary somewhat, so these instruments must be calibrated by studying the flow of a liquid of known viscosity.[18]

A chart is given in Figure 27 [19] that will be found useful in the

[15a] For a discussion of the expression for absolute viscosity, corrections for kinetic energy increase, and for information on the design of commercial viscosimeters, see Archbutt and Deeley, "Lubrication & Lubricants," and also the article by Winslow H. Herschel in *Trans. Am. Soc. Civ. Eng.*, 84 (1921), 527-50.

[16] Flowers, *Proc. Am. Soc. Test. Mat.*, 14 (1914), 565.

[16a] U. S. Bur. Stds., "Tech. Paper No. 112," p. 7.

[17] Herschel, W. H., "Tech. Paper No. 164," U. S. Bur. Stds., June 18, 1920, 5.

[18] Hershel, W. H., "Tech. Paper No. 112," U. S. Bur. of Stds. (1919).

[19] "Lubrication," May, 1921. (Published by the Texas Co.)

conversion of viscosities as determined by one instrument into the values that would be obtained by the use of other instruments, or for

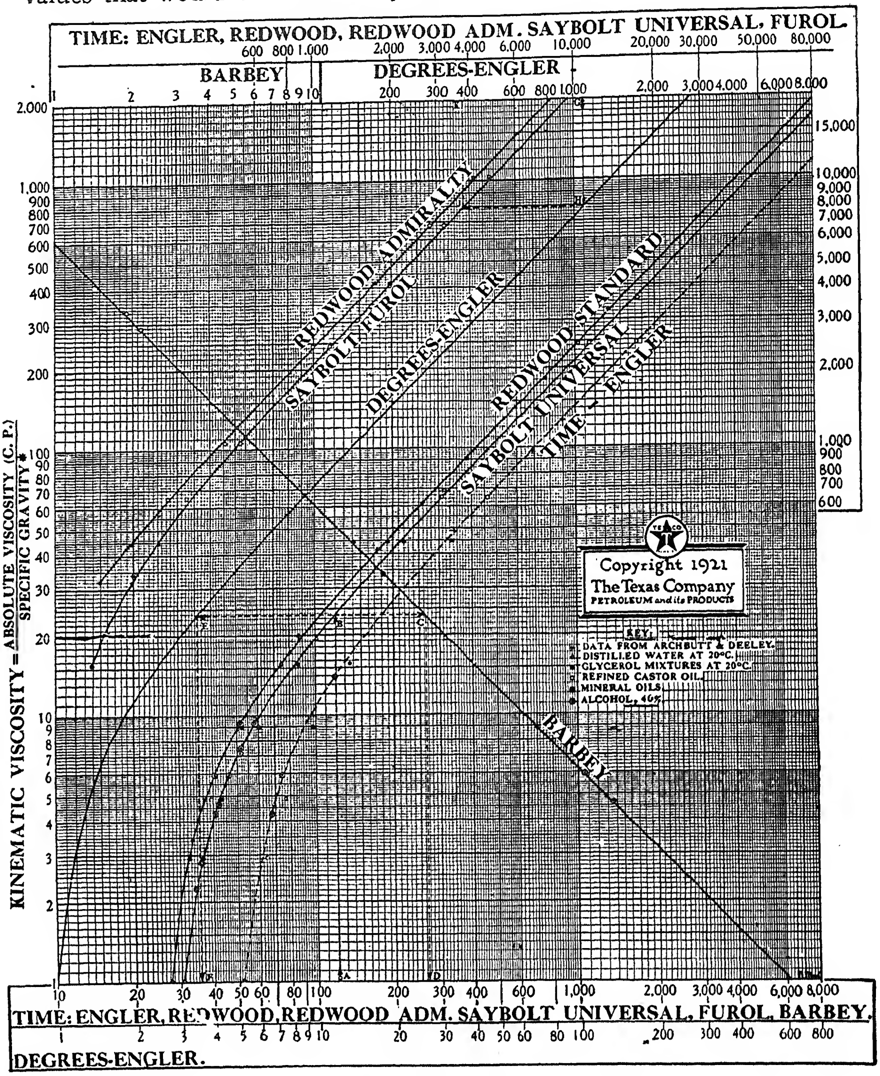


FIG. 27.—Viscosimeter Conversion Chart.

finding the equivalent kinematic viscosity in centipoises. Directions for using the chart are given thereon.

The viscosity of liquids decreases with temperature. In plotting curves showing the relationship of viscosity and temperature it will be

found convenient to use a logarithmic paper. The relationship between Saybolt viscosity and temperature will be found to be a straight line. Hence, if the Saybolt viscosity is determined at 100° F. and at 210° F., the Saybolt viscosity at any other temperature can be read from the curve. The experimental work should be carefully checked at 210° F. for a small error in the Saybolt viscosity taken at this temperature will change the slope of the line materially.

Velocity.

The velocity referred to is the mean-velocity and should be expressed in feet per second. The velocity may be calculated from data obtained in terms of the flow in gallons per minute by means of the expression:

$$v = \frac{0.408\ Q}{D^2}$$

If it is not desired to make this conversion the pressure drop may be expressed in terms of the flow by modifying Fanning's equation thus:

$$P = \frac{0.0538\ f\ l\ s\ Q^2}{D^5}$$

That is, in place of the factor $\frac{Dvs}{z}$ another, $\frac{0.408\ Q\ s}{D\ z}$, must be calculated.

Pressure Drop.

The pressure drop should be expressed in pounds per square inch. The theoretical horse power required may be calculated from the expression

$$H.P. = \frac{19.2 \times Q \times P}{33{,}000}$$

The conversion factors given in Table XXIX will be found convenient.

TABLE XXIX

CONVERSION FACTORS

X	To Convert "X" to Lbs./Sq. In. Multiply by	To Convert Lbs./Sq. In. to "X" Multiply by
Lbs./sq. ft.	0.00695	144.0
Centimeter of mercury	0.1934	5.171
Atmospheres	14.7	0.06804
Liquid head in feet ...	0.4332 s	$\frac{2.309}{s}$

Making Calculations.

With the values of the variables at hand the calculation of the pressure drop is a simple matter.

1. Calculate the value of $\frac{Dvs}{z}$, or, if Q is known rather than v, its equivalent $\frac{0.408\ Q\ s}{D\ z}$.

2. Refer to the lower curve of Figure 24 and find the value of "f" that corresponds to this value of $\frac{Dvs}{z}$ or $\frac{0.408\ Q\ s}{D\ z}$. Read from the curve that represents values of "f" for a pipe of roughness equivalent to that of the pipe to be used.

3. To find the allowance to be made for each ell refer to the upper curves of Figure 24. Use the value of $\frac{Dvs}{z}$ calculated as directed in (1) above. Multiply the value obtained from Figure 24 by the number of ells and then convert from pipe diameters to linear feet. Add this to the length of straight pipe. (In making these calculations note that two ells close together, or a return bend, have less effect than two ells several feet apart.)

4. Substitute the numerical values for the symbols in Fanning's equation:

$$P = \frac{0.323\ f\ l\ s\ v^2}{D} \text{ or the equivalent } P = \frac{0.0538\ f\ l\ s\ Q^2}{D^5}$$ and evaluate the pressure drop. The above calculations apply for both viscous and turbulent flow.

If "P" is known the equation may be transposed to find an expression equal to any of the other quantities.

If z is unknown, as in a calculation of how hot an oil must be heated to obtain a given discharge, calculate the permissible value of "f" from Fanning's equation. Refer to Figure 24 and find the corresponding value of $\frac{Dvs}{z}$. Equate this to $\frac{Dvs}{z}$ and solve for z.

The calculation is somewhat more complicated if D, v, or s is unknown, since these values occur both in Fanning's equation and in the expression $\frac{Dvs}{z}$ used in evaluating "f." The mistake of assuming $f = \frac{Dvs}{z}$ must not be made, for "f" is a function of $\left(\frac{Dvs}{z}\right)$ and not equal to it.

A cut and try method may be used by assuming a reasonable value for "f." A more satisfactory method is to assume a value for the unknown and solve for "p" in the ordinary way. If the value for "p" is too high or too low assume another value for the unknown. A value will soon be found that will give the desired "p." If the first approxi-

mation shows that the flow is viscous the simplest method will be to substitute the known quantities into Poiseuille's equation

$$p = \frac{0.000668\ z\ l\ v}{D^2}$$

or its equivalent

$$p = \frac{0.000273\ z\ l\ Q}{D^4}$$

Limitations in the Application of Recommended Method of Calculations.[20]

1. The method is not directly applicable to the flow of gases where the drop in pressure in the pipe line is more than 10 to 15 per cent of the final absolute pressure, for in this event the density and velocity of the gas are changed. If, however, average values are used for density and velocity, rather than initial or final values, the method of calculation may be applied in cases where the pressure drop is as much as 40 to 50 per cent of the final absolute pressure. For calculations of pressure drop in compressed-air lines, in which the pressure drop is larger than this, a modified equation of W. K. Lewis [21] may be used. All ordinary calculations involving the handling of air in circular ducts, or steam in pipe lines, may be made by the regular method.

2. The method cannot be applied in the calculation of flow phenomena in short tubes that open into large chambers. The reader is referred to Herschel's [22] comprehensive treatment of this subject. The entrance and exit losses are important in flow through short tubes. These losses are of little consequence if the length of the pipe is over 1000 diameters. Approximate calculations can be made for phenomena in pipes no longer than 300 diameters.

3. The flow of such semi-plastic materials as asphalt or viscous colloidal solutions cannot be made by the method outlined.

4. Accurate calculations cannot be made if the pipe is badly corroded or pitted. The value of "f" may be twice that found from Figure 24.

5. If the fluid is hot, and is exposed to cooling, the existence of a large temperature gradient makes accurate calculations almost impossible. On the subject of pipe-line transportation of hot oil see Barrett, L. L.[22a]

6. The precipitation of solids such as paraffin wax, gummy substances, and so on, will greatly modify the flow.

If the calculations are made with these limitations (and others that may arise in special cases) in mind, the method is applicable to

[20] Wilson, McAdams, and Seltzer.
[21] *J. Ind. Eng. Chem.*, 8 (1916), 1133.
[22] *Trans. Am. Soc. Civ. Eng.*, 84 (1921), 527-50.
[22a] *Chem. Met. Eng.*, 24 (1921), 1148-52.

the accurate solution of problems connected with the flow of either gases or liquids in commercial pipe lines.

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The Transfer of Heat.

The transfer of heat from one fluid to another directly, or through a separating wall of some nature, is a matter of importance in the design and operation of almost every apparatus used in the oil refinery. The subject matter that follows is a review of the more important work in this field that has come to my attention.

I am impressed with the fact that the general conclusions of investigators in this field should be critically studied with the greatest care before they are used as a basis for the design of important equipment. The number of variable factors involved in heat transfer phenomena is so large that experimenters may easily have overlooked one or more. Under these circumstances fallacious assumptions are easily made, and plausible conclusions drawn.

The reviews of Hausbrand,[23] Badger,[24] Lucke,[25] Kreisinger and Ray,[26] Orrok,[27] W. K. Lewis,[28] et al, and others have been freely drawn on in preparing the following discussion. The reader is referred to these sources for fuller information as well as to the many original articles cited.

Heat may be transferred from one body to another by one or more of three processes:

1. Conduction.

This process involves a flow of heat from one point at higher temperature to another at lower temperature through one or more bodies. The particles of the substances of which the bodies are composed are not appreciably displaced. The temperature difference between the two points divided by the distance is called the temperature gradient. It is uniform only if there is no discontinuity in the conducting system.

2. Convection.

The movement of heated material from one point of a system to another point at a different temperature or of different heat capacity results in transfer of heat. The process is called convection, and involves translatory motion of matter. Wind is a typical convection current.

3. Radiation.

A hot body loses heat in the form of energy known as radiation. This is a vibratory disturbance or wave motion of the ether. The heat

[23] "Verdampfen, Kondensieren, und Kuhlen," Verlag Julius Springer, Berlin, 1920.

[24] "Heating and Evaporating Apparatus." *Michigan Technic,* March, 1919.

[25] "Engineering Thermodynamics," McGraw-Hill, N. Y., 1912.

[26] *Bull. No. 18,* U. S. Bur. of Min. "The Transmission of Heat into Steam Boilers." 1912.

[27] *Trans. Am. Soc. Mech. Eng.,* 1910.

[28] Vol. 57, No. 33—*Bull. Mass. Inst. Tech.*

energy received by the earth from the sun is of this type. Radiant energy passes through a vacuum with the velocity of light; it travels in straight lines, its direction is changed by mirrors, prisms or lenses, or in short it is qualitatively indistinguishable from light in all its properties. Some bodies, as for example sooty carbon, absorb radiation almost quantitatively, in which event the energy appears as heat. Other bodies absorb part of the radiant energy and reflect part, while still other substances, such as some of the gases, absorb very little.

All three of these processes[28a] are of importance in analyzing the heat transfer phenomena of a boiler furnace, of a pipe-still furnace, and in fact of any process carried out at temperatures above 750 to 900° F. At lower temperatures than these radiation is of much less importance than conduction and convection.

Typical Heat Transfer Processes.

From a commercial standpoint the five important typical heat transfer processes may be designated as follows. (The double arrows indicate that it may be desired to transfer heat in either direction.)

	Heat Transfer	Examples
1.	Gas ⇄ Solid	Hot flue-gases to solids in all types of furnaces. Recuperators, Regenerators, Economizers, Superheaters, Compressors, Intercoolers, Automobile "radiator," Brine-coolers.
2.	Gas ⇆ Liquid	Some scrubbers. Cooling towers. Distillation Columns. Absorption Columns.
3.	Liquid ⇆ Solid	Heat Exchangers. Condensers. Coolers. Automobile "radiator." Brine-coils.
4.	Condensing Vapor → Solid	Condensers. Fractionating-Condensers or Dephlegmators.
5.	Solid → Boiling Liquid	Stills. Pipe-stills. Boilers. Evaporators. Ammonia or CO_2 expansion coils.

The transfer of heat from gas to gas, and liquid to liquid, involves ›lete fluid miscibility as a result of convection and diffusion. No al problem of heat transfer is presented by these cases.

[8a] Royds, R., "Heat Transmission by Radiation, Conduction and Convection," Nostrand, 1921.

The bodies taking part in the heat transfer process may be stationary or may be relatively in motion. The movement may be parallel or countercurrent. The temperature of one body may remain constant when the other changes, or the temperature of both bodies may change. The nature of these process possibilities is pictured as in Figure 28. Examples of each type process are:

Process I. Heating an oil with constant-pressure steam.
Process II. Evaporating water under constant pressure in a boiler.
Process III. Parallel flow in interchangers.
Process IV. Countercurrent flow in interchangers. Heating an oil in a pipe-still.

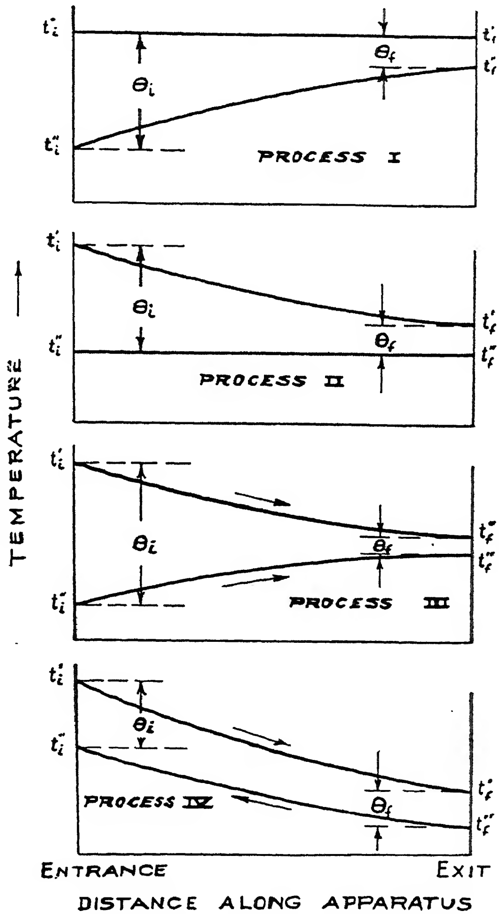


FIG. 28.—Typical Heat Transfer Process.

The curves help in visualizing the important features of each typical process. For example, it is evident that in processes involving *parallel flow* of two fluids the transfer of heat will be rapid at the start but slow at the end. The temperature of the cold fluid cannot be raised above the temperature at which the warmer fluid leaves the apparatus. If the flow of the fluids is *countercurrent* the cold fluid may be heated well above the temperature at which the warmer fluid leaves the apparatus. Thus, it is apparent that countercurrent flow should be used when it is desired to transfer as much heat as possible from the warmer fluid, and to raise the temperature of the colder fluid as much as possible. For example, the flow of oil in a pipe-still and flue-gas outside the pipes should be countercurrent. On the other hand, if it were desired to extract only a part of the heat from the warm fluid

in a small interchanger, the flow of the fluids should be parallel. The use of heat exchangers in cooling heavy Mexican residuum is an example of such a case. If too much heat is abstracted from the oil it becomes so viscous that it cannot be easily handled.

Nomenclature.

The following nomenclature is used in this discussion except as is otherwise indicated in the context. With the exception of the letter Θ the symbols are alphabetically arranged.

A = Suitable average area of heating surface in square feet.
A_c = Cross-sectional area in square feet of pipe, tube or conduit.
B = A variable in Jordan's film coefficient formula.
C = Various constants or coefficients.
C_p = Specific heat of gas at constant pressure, or B.t.u. per pound per degree Fahrenheit.
D = Inside diameter of pipe in inches (*Actual* and not nominal diameter).
f = fluidity $= \frac{1}{\text{viscosity}}$. If viscosity is in centipoises, the reciprocal is the specific fluidity with reference to water, for the viscosity of water at 20° C. is 0.0100 centipoises.
h = Film coefficient of heat transfer as B.t.u. per hour per square foot film area per degree Fahrenheit drop in temperature between the body of the fluid and the metal surface.
H = Over-all coefficient of heat transfer as B.t.u. per hour per square foot suitable average area of heating surface per degree Fahrenheit over-all temperature difference.
k = Absolute thermal conductivity of fluid or metal as B.t.u. per hour per square foot per degree Fahrenheit per foot thickness. Values of k can be obtained from tables of physical constants and from various handbooks.
M = Average molecular weight of the fluid.
Q = Quantity of heat transferred per hour.
r_h = Mean hydraulic radius or $\frac{\text{area conduit}}{\text{perimeter}}$.
s = Specific gravity of the fluid at the working temperature and pressure in $\frac{\text{lbs. per cu. ft.}}{62.3}$
S = Shape factor = Area of the heating surface in square feet divided by free volume of apparatus in cubic feet. S equals the reciprocal of the hydraulic radius taken in feet.
t = Temperature in degrees Fahrenheit.
t_1 = Initial temperature in degrees Fahrenheit.

t_f = Final temperature in degrees Fahrenheit.
t' = Temperature of 1st fluid in degrees Fahrenheit.
t'' = Temperature of 2nd fluid in degrees Fahrenheit.
t_m = Arithmetical mean temperature.
T = Absolute temperature in degrees Fahrenheit = degrees Fahrenheit + 460.
Θ_i = Initial temperature difference between two fluids in degrees Fahrenheit.
Θ_f = Final temperature difference between two fluids in degrees Fahrenheit.
Θ_m = Mean temperature difference between two fluids in degrees Fahrenheit during change from initial to final conditions.
u = Average linear-velocity of fluid in feet per second = cubic feet per second divided by average clear cross-sectional area in square feet.
v = Average mass-velocity of fluid as lbs. fluid per second per square feet of average clear cross-sectional area.
w = Weight of fluid flowing in pounds per second.
x = Per cent steam by volume $= \dfrac{100:\text{partial pressure of steam}}{\text{total pressure of mixture}}$.
z = Viscosity of fluid in centipoises (i.e., 0.01 c.g.s unit of viscosity). The viscosity of water at 68° F. = 1 centipoise. Hence z is also the viscosity of fluid relative to water at 68° F. "z" is a function of the temperature. For water the value of z at any temperature between 70° F. and 180° F. may be calculated from the equation:

$$\frac{1}{z} = -0.12 + 0.0161\ t$$

Transmission of Heat from a Hot Gas to a Liquid within a Metal Tube.

The transfer of heat from a hot flue gas through a metal tube to a liquid may be taken as a common case that will serve very well as a basis for preliminary discussion. The flow of heat is proportional to the mean temperature difference Θ_m and to the area of the heating surface A, or

$$Q = H\ A\ \Theta_m$$

Mean Temperature Difference.

If the curves shown in Figure 28 were straight lines the mean temperature difference would be the arithmetic mean of Θ_i and Θ_f. However, if the flow of heat is strictly proportional to the temperature difference the curves in Figure 28 are of exponential type. (Except of course, when temperature is constant.) Hence the mean temperature difference is given by the expression:

$$\text{Mean temp. diff.} = \frac{(\text{Initial temp. diff.}) - (\text{Final temp. diff.})}{\log_e \left[\dfrac{\text{Initial temp. diff.}}{\text{Final temp. diff.}}\right]}$$

or,

$$\Theta_m = \frac{\Theta_i - \Theta_f}{\log_e \dfrac{\Theta_i}{\Theta_f}} = \frac{\Theta_i - \Theta_f}{2.3026 \log_{10}\left(\dfrac{\Theta_i}{\Theta_f}\right)}$$

The proportionality factor "H" is called the over-all coefficient of heat transfer and is here expressed as the B.t.u.'s transferred per square foot of suitable average heating surface per hour per 1° F. difference in temperature. Q is given therefore in B.t.u. per hour. The over-all coefficient of heat transfer H is a complicated function of the velocity, or more probably of the mass-velocity, of each fluid, the nature of the apparatus, the conductivity of the fluids and the metal, and of the condition of the heating surfaces.

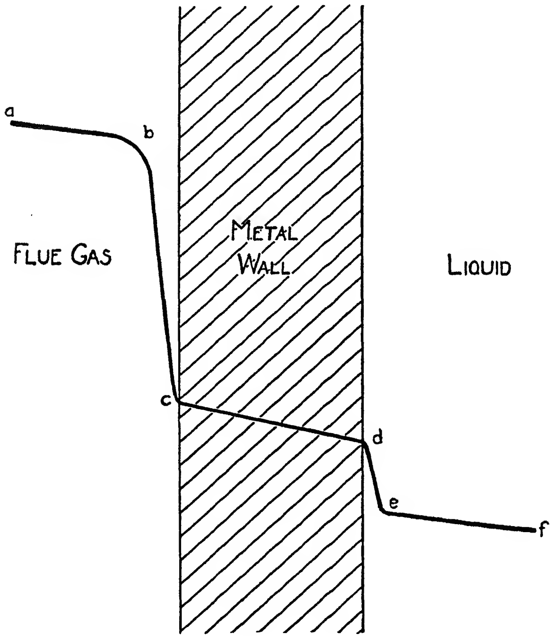


FIG. 29.—Temperature Drops.

The anomalies of heat transfer calculations are wrapped up in the over-all coefficient H, and only when this coefficient is picked apart and the variable factors involved thoroughly investigated will it be possible to make even approximately accurate calculations of heat transfer. The only alternative to an analysis of H is the determination of a coefficient H for every individual apparatus and operation. This latter procedure is essentially the one that has been followed by most engineers. Values of H may vary from 0.4 to over 1000.

The coefficient H is the reciprocal of the resistance to heat flow. The over-all resistance may be thought of as the sum of several resistances. The diagram presented as Figure 29 is helpful in picturing the phenomena of heat transfer.

The hot flue-gas is moving along the tube wall on one side, and the liquid that is being heated on the other. The body of the flue-gas and of the liquid has some definite velocity. On each side of the metal wall there exists a film of fluid moving with a velocity that varies from a value zero next the tube wall to the velocity of the body of the fluid at some distance from the tube wall. Hence, in order that heat may pass from one fluid to the other it must flow through the two fluid films. The heat conductivity of gases and liquids is very small as compared to that of solids. If the conductivity of N_2 and CO_2 is unity, the conductivity of a paraffin base oil is 7, water 26, gas carbon 200, wrought-iron 2,900 and copper about 19,500. It is apparent therefore, that the thermal resistance of the metal is only a small factor (unless the metal is very thick or the fluid flow very rapid) in the over-all resistance to heat flow, and that the important factors are the resistances of the fluid layers or films next the metal. This is known as the film concept of heat transfer.

However, it should be carefully noted that it is incorrect to conceive of the fluid film as offering the only resistance of the fluid to heat flow from it to a metal wall. The papers of Osborne Reynolds on what may be called convective resistance to heat flow should be consulted on this point. Reynolds' reasoning has been presented recently in an excellent editorial[28b] discussion of heat transfer. Because of a general misconception in regard to "film coefficients" the following quotation from this editorial is included here.

"Reynolds' reasoning may be put in the following form. Let us neglect for the moment the existence of the thin film of non-turbulent fluid which slides along the inner surface of a condenser tube. In the absence of this film the flow is wholly turbulent, and thus a particle of the fluid which at one instant is at the center of the tube where its momentum is, say, mv_o, and its temperature t_o, is at the next moment hurled against the wall of the tube where it is brought to rest, or, in other words, acquires the momentum of the wall, which is zero.

"At the same time it also acquires the temperature of the wall. To simplify matters we may suppose the wall to be colder than the fluid, and then it will be seen that heat is transferred to the wall in exactly the same way as momentum is, and the rate at which the difference of temperature is destroyed is proportionally exactly the same as the rate at which momentum is destroyed. The latter is measured by the loss of head in the length of pipe considered, and as this is known from experiments on pipe friction, a mathematical relationship can be established between the pressure gradient along the tube, the temperature gradient along the tube, and the difference of temperature between wall and water.[28c]

[28b] *Engineering*, 107 (1919), 145-6.

[28c] The expression obtained is: (Not translated into the nomenclature used in this chapter) $T-t=\frac{d}{4L}\cdot\frac{dt}{dx}$ where T denotes the wall temperature, t the mean temperature of the water at the point considered, d the diameter of

"In actual practice, of course, the flow never is fully turbulent, so that what Osborne Reynolds' theory gives us is the temperature of the inner face (i.e., face nearest the axis of the pipe) of the non-turbulent film. This temperature is considerably higher than that of the general mass of the circulating water. Thus in one of the exceptionally careful experiments of Mr. J. A. Smith[28e] the conditions were a 6 ft. tube with a cross-section of 0.26 sq. in. surrounded by air-free steam, at a temperature of 110° and traversed by circulating water, which entered at 67° F. and left at 86° F. so that its mean temperature was about 78° F. From Reynolds' theory we find that the temperature of the inner surface of the non-turbulent film averaged about 86° F., and as the temperature of the tube wall was probably about 106° F. (the steam being air-free) we find that in this case the convective resistance was responsible for fully one-quarter of the total heat-drop between tube and circulating water."

It is thus seen that the resistance ordinarily referred to as the "film-resistance" is in reality the sum of the *actual film resistance* and a convection resistance. The usual assumption that "film-resistance" is directly proportional to film thickness and inversely proportional to the conductivity of the fluid is not strictly true. It is impossible to measure the exact thickness of the fluid film, so the effect of the several variable factors is included in a constant "h," and the resistance to heat flow offered by the fluid is given by the expression $\frac{1}{h\ A}$. The "film coefficient" "h" is not the real conductance of the film, but the symbol "h" will be used and called the film coefficient. The real significance of "h" should, however, be kept in mind.

The film coefficient "h" is found to be nearly proportional to the mass-velocity and heat conductivity of the fluid, and inversely proportional to the viscosity of the fluid. The proportionality to the mass-velocity (Jordan and Reynolds), that is, to the weight of fluid flowing per unit of cross-sectional area per unit of time, rather than to the linear velocity, should be noted in particular. This may account in part for the many discrepancies noted in comparing the work of investigators who have used identical velocities, but in whose experiments one or more of the factors, temperature, density, or cross-sectional area, may have been different.

However all this may be, one must not become too enthusiastic

the tube in centimeters, and $\frac{dt}{dx}$ the temperature gradient along the tube, whilst L denotes Lee's[28d] function:

[28d] Lee's "On the Flow of Viscous Fluids Through Smooth Circular Pipes." *Proc. Roy Soc.*, London, 91 (1914), 46-52.

$$L = 0.765 \left(\frac{V}{vd}\right)^{0.35} + 0.0009$$

V being the kinematic viscosity of water, v its velocity in centimeters per second, and d the diameter of the tube in centimeters.

[28e] Proc. Victorian Institute of Eng., VI, *Engineering,* March 23, 1906, 395.

over film coefficients as a panacea for all the difficulties of heat transfer calculations. They are a step in the direction of a more certain determination of the values of some of the variables involved, but as in the case of Mr. Wilson's famous fourteen points there may be an unreckoned fifteenth. Lucke comments on this phase of the subject in his "Engineering Thermodynamics" (1912). Speaking of the development of a general heat transfer law he says, "This ultimate aim appears, however, to be quite hopeless of attainment, and even if it were not without hope it would probably be useless, because any general law

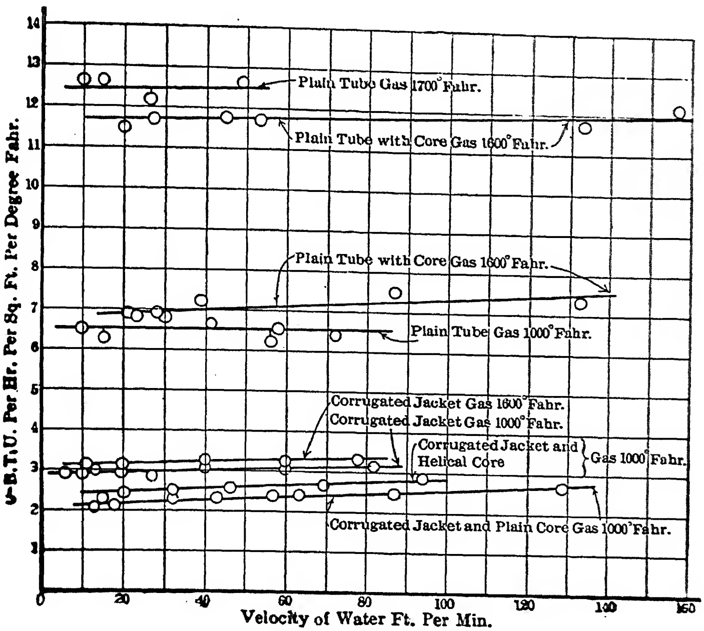


FIG. 30.—Effect on "H" of Changing the Velocity of the Fluid of Low Thermal Resistance.

must include terms to account for the conditions of surface, the gas content of liquids and vapors, something equivalent to the thickness or resistance of fluid films, and other things equally indeterminate. . . ."

"About all that one could reasonably expect in this connection is a relation of H to the definable variables in each characteristic class of heat transfer, with perhaps a few general principles; and some of these principles are fairly well established, though none quite beyond the limits of controversy."

It may never be possible to formulate a general law that can be used in the exceedingly accurate design of heat transfer apparatus

because of variability of the conditions affecting the apparatus in use. But it is surely worth while to understand in a quantitative way as many of the variables as possible. The fewer the factors that are imperfectly understood the closer the guess as to their effect and the necessary allowance therefor.

When heat is to be transferred from a hot gas to a liquid flowing in tubes the main resistance to flow is that of the gas film. The rate of transfer is practically controlled by the high resistance of the gas film.

All observers agree in assigning higher values to H when the rate of flow of the fluid having the high resistance to heat transfer is increased.

If the resistances of the fluid films on each side of the metal wall are of comparable magnitude, the value of H will be larger the more rapid the flow of both fluids. The small effect of changing the velocity of the fluid of low thermal resistance is shown in Figure 30.[29] Values of H are plotted as ordinates ("H" is same as Lucke's "U"). The velocity of the water in the tubes had little effect on the over-all heat-transfer coefficient, but changes in the nature of the heating surface on the gas side, and changes in gas temperature, had pronounced effects. Whether the effect of temperature change is to be ascribed to this change as such, to the necessarily increased gas velocity, or perhaps to change in density, was not determined. The jacketed tube referred to in the figure consisted of the plain tube covered with cast-iron Foster superheater rings. Lucke's method of calculation of the heating surface is not entirely clear.

Nearly fifty years ago, Osborne Reynolds[30] predicted on theoretical grounds that the rate of heat transfer would be a linear function of the product of the density and velocity of a fluid. This product may be called the mass-velocity and is equal to the weight of fluid flowing per unit time per unit of cross-sectional area. Experiment has failed to confirm Reynolds' prediction, however. The quantity $\left(\frac{W}{A}\right)$ is used by Nusselt with an exponent 0.786 and by Brabbee with an exponent 0.79.

The Transfer of Heat: Gas ⇄ Solid.

The transfer of heat from gases to metal surfaces or vice versa is an important engineering operation, and has been the subject of numerous experimental investigations. These are too extensive to be reviewed here in detail. The most important work is that of Nusselt,[30a] who passed air, at various pressures up to 214 lbs./sq. in. gage, through a brass tube of 0.87-inch inside diameter and 1.02-inch outside diameter. The tube was surrounded by a steam-jacket held at 215° F. Nusselt's equation is

[29] Lucke, "Engineering Thermodynamics," p. 559.
[30] "Collected Scientific Papers," 2 vols., Cambridge Univ. Press.
[30a] *Mitteilungen Forschungs-arbeiten,* No. 89 (1910).

$$h = 26.9 \frac{k_{(wall)}}{D^{0.214}} \left(\frac{u\ C_p}{k_{(gas)} \cdot V_S} \right)^{0.786}$$

in which all of the symbols have been defined except V_S which is the specific volume in cubic feet per pound of gas.

A simplified form of Nusselt's equation is—

$$h = b \left(\frac{W}{A} \right)^{0.786}$$

in which "W" is pounds of gas per second and A the area of the gas path in square feet, and

$$\begin{aligned} \text{"b"} &= 0.00114 \text{ for air} \\ &= 0.00094 \text{ for } CO_2 \\ &= 0.00213 \text{ for steam, or} \\ &= 0.00306 \text{ for coal gas} \end{aligned}$$

This is applicable to cases in which gases flow inside tubes of about 1″ diameter with steam outside at moderate pressures.

Professor W. L. Badger has recalculated the work of the various investigators in order to allow comparison of all data. I am advised by him that the results of Nusselt,[31] Ser,[32] Josse,[33] Bell,[34] Royds and Campbell,[35] Royds,[36] and Brabbée [37] are in fairly good agreement. If these are plotted using "h" as ordinates and values of $\frac{W}{A}$, that is, pounds of gas per square foot per second, as abscissas, the equation of the line that represents the average of these data is $h = 4.32 \left(\frac{W}{A} \right)^{0.75}$ which I shall call Badger's equation. No account is taken in this relationship of the shape factor, of mean working temperature, or of those factors, such as specific heat, that are dependent on the nature of the gas. Such niceties are not justified in the present state of knowledge. Badger's equation is properly restricted in its application to air flowing inside tubes of ½″ to 2″ diameter at velocities higher than the critical, and at temperatures less than 400° F. For gases other than air Nusselt's equation should be used.

In a qualitative way it is readily seen that increase in the shape factor decreases the value of "h," and that since the thermal conductivity of gases increases with temperature, "h" will be greater the higher the film temperature.

[31] *Loc. cit.*
[32] *Traité de Physique Industrielle,* 1888.
[33] *Engineering,* 86 (1908), 802–6.
[34] *Mech. Eng. Sec. Int. Eng. Cong.,* 1915.
[35] *Trans. Inst. Eng. Shipbuilders in Scotland,* 55 (1912), 153-207.
[36] *Ibid.,* 58 (1915), 155-211.
[37] Mitteilungen Prüfs-Anstalt für Heizungs und Luftungs Anlagen. Heft 3, 1910. Abstracted by Hausbrand in "Verdampfen, Kondensieren, und Kuhlen," 7th Ed., p. 114.

Other investigators whose work is not in agreement with that already cited are Nicholson,[38] Jordan,[39] Kreisinger and Ray,[40] and Lewis, McAdams and Frost.[41] Of these the work of Lewis, McAdams and Frost conforms more closely to the large group that were in fair agreement than any of the others, but their values of "h" are higher than those given by Badger's equation. The equation given by Lewis, et al., is

$$h = \frac{0.88v^{0.8} . C_P \cdot \sqrt{T} . S^{0.2}}{M^{0.8}}$$

and the claim is made that it is applicable to any case in which a gas is flowing in a turbulent manner inside a pipe. This formula was based on a critical comparison of the data of Nusselt, Josse, Jordan, Fessenden, Babcock and Wilcox, and others, and in form is very similar to that of Nusselt. Data covering the flow of CO_2, air and illuminating gas in pipes of ½-inch to 2-inch diameter were used in deriving the expression. Mass-velocities were varied from 1 to 20 lbs. per sec. per sq. ft. transverse area of the tube, and temperatures from 70 to 2000° F. Lewis, et al., claim that the results of calculation with this formula check closely with isolated experimentally determined values of "h" for pipes up to 12 inches in diameter. The observed values of "h" were somewhat higher than those calculated by the formula.

The general formula can be simplified if it is to be applied to a given gas. For air at ordinary temperatures in 1-inch to 2-inch pipes $h = Cv^{0.8}$ where C varies from 3.7 to 4.5. The value for air of 200° F. average temperature and in a 1-inch pipe is 4.2.

When the gas is outside of and flowing at right angles to staggered pipes, Lewis, McAdams and Frost use a modified formula:

$$h = \frac{3.28\ v^{0.8}\ C_P \cdot \sqrt{T} \cdot S^{0.2}}{M^{0.3}}$$

This equation has been tested only on the flow of air.

Carrier's[42] formula, used in the calculation of heat transfer in air-heaters, may be useful in some cases. The air flows at right angles to the 1-inch pipes of the heater. The pipes were spaced in such a manner as to give about 50 per cent clear area. The air film coefficient is given by the expression:

$$h = \frac{22.3\ V_C}{1.42 + V_C}$$

[38] *Junior Inst. of Eng.*, 1908.
[39] *Proc. Inst. Mech. Eng.*, 1909, II, 1317-57.
[40] U. S. Bur. of Min., *Bull. No. 18* (1912).
[41] *Bull Mass. Inst. Tech.*, 57, No. 33, Contribution from Dept. Chem. Eng. Ser. No. 4, 1922.
[42] *Trans. A. S. M. E.*, 33 (1911), 1055-1136.

in which V_C is the mass velocity at the center line of pipes in the same row. The values of V_C varied from 0.25 to 1.50 lbs. per sec. per sq. ft. of minimum free air. The corresponding values of h were 3.34 to 11.5 B.t.u. per hr. per 1° F. per sq. ft.

The heat transfer in tempering coils has also been studied by Rietschel,[43] Brabbee,[44] and Harrison.[45]

A detailed critical review of the entire subject of heat transfer has been made by Professor Badger of the Chemical Engineering Department of the University of Michigan and will be available as part of the subject matter of his work on evaporation which is soon to be published. The reader who is interested in heat-transfer will do well to refer to Professor Badger's book.

The Transfer of Heat: Gas ⇄ Liquid.

The direct transfer of heat from gases to liquids or vice versa has received so little attention at the hands of investigators that it is quite impossible to discuss the subject. Reference should be made to a recent paper [46] by W. G. Whitman and J. L. Keats.

The Transfer of Heat: Liquid ⇄ Solid.

The transfer of heat from a liquid to a solid or vice versa is of such importance that the limitations of present knowledge of the subject are to be deplored. The fact is that the results of various investigators are not in accord.[47] However, they are briefly reviewed here in order to indicate the general nature of the work. The original articles should be consulted and carefully considered before any application of importance is made of formulas or data.

In many instances of transfer of heat from a gas through a solid to a liquid, the thermal resistance of the solid and of the liquid film may be neglected. However, if the temperature drop is small, the velocity of the gas high, and that of the liquid low, the resistance of the liquid film is important. Also the resistance of liquid films is the basis of design of heat interchangers and coolers.

A paper entitled "Passage of Heat between Metal Surfaces and Liquids in Contact with Them" was published by T. E. Stanton [48] in 1897. The paper was based on experiments in which streams of water were passed in the same direction through an apparatus consisting of an inner tube and a jacket tube. One stream of the liquid flowed through the inner tube and the other in the annular space between the

[43] *Leitfaden z. Berechner u. Entwerfen Luftungs u. Heizungs-anlages.*
[44] *Loc. cit.*
[45] *Heating and Ventilating Mag.*, Oct. and Nov., 1907.
[46] *J. Ind. Eng. Chem.*, 14 (1922), 186-191.
[47] Professor Badger has recalculated and critically studied the results of various investigators. I am informed by him that there is so little similarity that it is impossible to draw any general conclusions.
[48] *Phil. Trans. Roy Soc., London,* 190 (1897), 67-88.

two tubes. The work is too lengthy to be given in full here, and the reader is referred to the original or to an abstract [48a] by Kreisinger and Ray. The heat transmitted from the surface of a pipe to water flowing in the pipe is given by the expression below. This has not been transformed so that engineering units may be substituted but is in the form given by Stanton

$$h = \frac{k}{4} \cdot \frac{P^{2-n}}{(2r)^{2-n}} (t_o - t)\ (1 + \alpha t_o)\ (1 + \beta t)\ u^{n-1}$$

in which

h = film coefficient of heat transfer expressed as small calories per second per square centimeter per 1° C. at some chosen cross-section.

k = a constant for a given pipe. The value of K varies with the diameter, length and nature of the surface of the pipe. Values are given below for a copper pipe.

P = a factor whose value decreases with rise in temperature in accordance with the expression

$$P = (1 + 0.0336\,t + 0.000221\,t^2)^{-1}$$

in which t is average temperature of the water in degrees Centigrade.

r = radius of the tube in centimeters.

n = an exponent that is equal to 1.835 for clean copper tubes and is not much different for other smooth tubes. For rough tubes n = 2.0.

t_o = temperature of inner surface of the pipe in degrees Centigrade.

t = temperature of the water at any particular cross-section in degrees Centigrade.

α = 0.0004.

β = 0.01.

μ = mean linear velocity of the water in centimeters per second.

Copper Pipes		Value of K			Number of Exps.
Diam. cm.	Length cm.	Maximum	Minimum	Mean	
1.39	47.0	0.0108	0.0104	0.0106	22
1.07	44.5	0.0104	0.0100	0.0102	13
0.736	46.0	0.0103	0.0099	0.0100	15

The transfer of heat per unit area of the pipe at any particular cross-section is seen to be dependent on the nature of the surface and the dimensions of the pipe, on a factor P, on the temperature difference

[48a] *U. S. Bur. of Min., Bull No. 18* (1912).

(between metal surface and water) multiplied by the factors $(1 + \alpha t_0)$ and $(1 + \beta t)$ that correct for the fact that heat transfer is not an exact linear function of temperature difference but that it increases somewhat (as indicated by the respective factors) both with increase of temperature of the surface of the metal and of the water, on the velocity raised to a power slightly less than 1, and on the reciprocal of the diameter (2r) raised to the power (2-n). Thus the rate of heat transmission is not quite doubled by doubling the linear velocity of the fluid nor by doubling the diameter.

The transfer of heat through the fluid film next the wall of the entire pipe cannot be exactly calculated by multiplying "h," as given by the equation above, by the area of the inside of the pipe. This can be obtained by a more exact integration of the expression for the slope of the curve representing the increase in the temperature of the water as it flows through the tube than that used in deriving the expression for "h" given above. The original article must be consulted for this as well as for a method of approximating the conductance of the entire film.

It should be noted that the transfer of heat from water to metal is not the same as that for metal to water under comparable conditions. The original article must be consulted on this. The transfer of heat from water to metal was found to be only approximately three-quarters as rapid as that from metal to water. This is not to be considered a general conclusion, as the pipe sizes, nature of pipes, and experimental conditions used by Stanton were limited. This latter phase of the subject should be investigated further.

The thermal resistance of a water film was studied by Clement and Garland.[49] Their apparatus consisted of a 1-inch Shelby cold-drawn steel tube (O.D. 1.253 in., I.D. 0.985 in.) surrounded by a steam jacket. The results of their experiments are reproduced in Table XXX. The "conductances" given in columns 15, 16, and 17 are the film coefficients expressed as B.t.u. per second per sq. ft. per 1° F. To obtain the values of "h" multiply conductances by 3600. The term "conductance" is used by them in contrast to "conductivity." The latter is a specific physical property of a substance and gives the property of a unit thickness, whereas "conductance" refers to any thickness. The reader should refer to the original publication for details of Clement and Haskins' work.

Following the work of Clement and Garland the next investigation of heat transfer phenomena in which the temperature of the metal wall was measured was that of G. C. Webster.[50] The main object of Webster's study was to determine the effect of various factors on the transfer of heat from steam to a tube wall. Less attention was paid to the phenomena on the water side of the tube. He failed to determine the temperature gradient along the tube on the water side.

[49] *Bull. No. 40,* Univ. of Ill., Eng. Exp. Sta., Sept. 27, 1909.
[50] *Inst. of Eng. and Shipbuilders in Scotland,* 57 (1913), 58-105.

TABLE XXX

DATA OF CLEMENT AND GARLAND

	Temperatures in Degrees F.										Water		Conductance				
No.	Entering Water Av.	Leaving Water Av.	Rise	Steam in Jacket	Steam Wall of Tube. Mean	Drop from Steam to Wall of Tube	Drop through Metal of Tube	Water Wall of Tube	Water in Tube. Mean	Drop from Wall of Tube to Water	Weight of Water per Minute	Velocity of Water in ft. per second	B. t. u. per sq. ft. per Minute	Conductance of Film on Steam Side	Conductance of Film on Water Side	Conductance of Tube and Film on Water Side	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	
1	56.92	66.75	9.83	210.9					61.8		318.0	16.07	1615				
2	58.20	70.25	12.05	210.9					64.2		263.0	13.29	1638				
3	58.55	71.90	13.35	210.9					65.2		236.0	11.93	1628				
4	58.33	73.20	14.57	210.9					65.9		204.3	10.33	1538				
5	58.20	74.82	16.62	210.9					66.5		176.0	8.90	1512				
6	57.89	75.28	17.39	210.9					66.6		147.0	7.43	1322				A
7	58.20	78.52	20.32	210.9					68.4		120.0	6.07	1260				
8	58.29	84.49	26.20	210.9					71.4		81.1	4.11	1098				
9	58.37	92.00	33.63	210.9					75.2		55.1	2.80	957				
10	58.91	108.40	49.50	210.9					83.7		29.0	1.48	741				
11	60.10	175.49	115.40	210.9					117.8		7.12	.37	425				
1	58.55	73.35	14.80	273.6	181.2	92.4	35.2	146	65.9	80	331.7	16.78	2537	.458	.528	.367	
2	58.32	78.12	19.80	274.4	202.0	72.4	34.7	167	68.2	99	244.4	12.37	2501	.576	.421	.312	
3	58.15	75.45	17.30	273.7	193.2	80.5	36.5	157	66.8	90	294.3	14.89	2631	.544	.487	.347	
4	57.90	80.94	23.04	273.9	203.0	70.9	33.1	170	69.4	100	200.5	10.15	2387	.561	.399	.300	
5	58.03	85.83	27.80	274.1	208.0	66.1	31.0	177	71.9	105	155.7	7.89	2237	.561	.354	.273	B
6	58.10	92.88	34.78	274.1	211.0	63.1	28.9	182	75.5	106.5	116.0	5.88	2083	.550	.325	.256	
7	62.87	120.46	57.59	274.1	235.0	39.1	23.8	211	91.7	119	57.6	2.94	1715	.730	.240	.200	
8	63.28	108.50	45.22	274.5	227.0	47.5	24.8	202	86.0	116	76.4	3.89	1786	.628	.256	.211	
9	63.73	145.90	82.17	274.5	239.7	34.8	21.0	219	105.0	114	35.7	1.84	1516	.724	.222	.187	
10	67.55	162.20	94.65	274.4	243	31.4	19.0	224	114.0	110	28.0	1.45	1369	.724	.207	.177	
1	67.54	85.00	17.46	306.6	219.9	86.7	43.6	176	76.3	100	348.4	17.64	3144	.605	.525	.365	
2	67.54	87.19	19.65	306.6	219.0	87.6	43.2	176	74.4	102	306.4	15.50	3112	.591	.508	.357	
3	67.54	93.30	25.76	306.5	230.5	76.1	41.6	189	80.4	109	226.0	11.43	2998	.655	.459	.333	
4	58.73	107.69	48.96	306.8	246.4	60.4	36.7	210	83.2	127	104.7	5.33	2649	.731	.347	.269	C
5	58.89	118.05	59.16	307.0	252.3	54.7	34.7	217	88.5	129	81.8	4.17	2501	.761	.322	.254	
6	59.27	129.70	70.43	307.0	255.7	51.3	31.3	224	94.5	129	62.0	3.17	2256	.731	.291	.234	
7	59.52	154.35	94.83	307.4	261.1	46.3	28.8	232	107.0	125	42.5	2.19	2081	.750	.278	.226	
1	57.67	80.50	22.83	330.2	220	110.2	55.2	165	69.0	96.0	338.4	17.13	3995	.606	.694	.440	
2	57.67	83.88	26.21	330.0	229.4	100.6	52.0	177	70.8	106.0	277.4	14.05	3756	.621	.591	.396	
3	58.28	90.92	32.64	330.0	233.1	96.9	47.8	185	74.6	110.0	205.0	10.39	3455	.594	.524	.365	D
4	58.17	97.90	39.73	330.2	241.8	88.4	45.1	197	78.07	119.0	158.7	8.06	3260	.614	.457	.331	
5	58.50	120.60	62.10	330.2	257.4	72.8	37.0	220	89.5	130.5	83.3	4.25	2672	.611	.340	.265	
6	58.89	161.50	102.61	330.2	267.1	63.1	32.8	234	110.2	124.0	44.7	2.31	2370	.625	.318	.251	

This, taken together with the fact that in some instances the temperature of the water was so high that the dissolved air was probably liberated, detracts from the value of his work. Webster's data are of interest, however, and should be kept in mind for comparison with future work. He concluded that the flow of heat from metal to water was directly proportional to the temperature difference between metal wall and water, multiplied by an expression to correct for the increase in diffusivity of the water with rise in temperature, and not directly proportional to the velocity of the water.

His formula for the transfer of heat from tube to water is

$$h = 60\ (A + 0.0573\ V)$$

in which

$$A = -5.5 + 0.24\left(\frac{\text{temp. tube wall}\ ^\circ\text{F.} - \text{Av. temp. water}\ ^\circ\text{F.}}{2}\right)$$

and V = velocity of water in feet per minute.

Webster's experiments have been reviewed and recalculated by A. W. Porter.[51] The data are presented in graphic form that greatly simplifies their practical application. However, the reader should refer to an editorial in *Engineering*[52] for a critical review of Dr. Porter's paper, and carefully weigh the comments made before accepting his conclusions.

The transfer of heat in double-pipe heat-exchangers has been studied by the Brown Company of Berlin, New Hampshire, and reported by Mr. George A. Richter,[53] who was in charge of the work. The inner pipes were made of lead, and varied in nominal size from 1-inch to 2-inch. The wrought-iron jackets varied in size from 2-inch to 4-inch. Hot water was circulated in the lead pipe, and cold water in the annular space between the pipes. Velocities and temperatures of the fluids were varied. In some experiments the coolers were made up of straight 20-foot lengths of pipe connected into a continuous coil with return bends. In other experiments the coolers were continuous helixes.

They conclude that a double-pipe interchanger of helical form conducts 10 to 20 per cent more heat than a comparable apparatus constructed as an assembly of straight tubes. The increase in pump pressure required to force the fluids through the helical coils is small in comparison to the increase in capacity for transferring heat. Substitution of a 2-inch pipe for a 1½-inch pipe within the 4-inch jacket pipe of a helical cooler increased the heat-transfer capacity, the latter apparently varying inversely to the ratio

$$\frac{\text{I.D of outer pipe} - \text{O.D of inner pipe}}{\text{I.D. of inner pipe}}.$$

[51] *Engineering*, 107 (1919), 125-6, 140-2.
[52] 107 (1919), 145-6.
[53] *Trans. Am. Inst. Chem. Eng.*, 12 (1919), 147-185.

The coefficient of heat-transfer increased slightly with increase of temperature. This is in accord with the findings of Stanton. The reader should refer to this paper for detailed information too voluminous for reproduction here. The value of the over-all coefficient H was expressed in terms of constants and the linear fluid velocities. The formulas are modifications of that of Molier, and may in general be written:

$$H = \frac{C_1}{\frac{1}{1 + c_2\ u_1^{n}} + \frac{C_4}{1 + c_3\ u_2^{m}}}$$

The values of the constants found by Richter are shown in Table XXXI.

TABLE XXXI

CONSTANTS IN RICHTER'S FORMULA

Constants	Cooler No. 1, 60 Ft. 1-in. Lead Pipe Within 3 Length 2 In. W. I. Pipe	Cooler No. 2, 60 Ft. 1-in. Lead Pipe Within a Helix of 2 In. W. I. Pipe	120 Ft. 1½ In. Lead Pipe Within a 4-Inch W. I. Pipe Helix	120 Ft. 2-In. Lead Pipe Within a 4-Inch W. I. Pipe Helix
C_1	62.7	76.2	57.5	80.0
C_2	5	5	5	5
C_3	5	10	10	10
C_4	1	1	2.6	2.6
n	0.57	0.60	0.57	0.60
m	0.57	0.50	0.57	0.50

Lewis, McAdams and Frost[54] give the following formula for evaluating the liquid film coefficient:

$$h = \frac{712\ c\ k\ u^{0.8}}{z\ m^{0.17}}$$

in which c is a cleanliness or roughness coefficient. The formula is claimed to hold for pipes of ½-inch to 2-inch diameter, and for calculations of film coefficients when the liquid is flowing in the annular space between a 2-inch and a 3-inch pipe as well as for smaller annular spaces. Fluid velocities ranged from 1 to 15 feet per second and values of "h" from 200 to 2000 B.t.u. per hour per square foot per 1° F.

The value of "c" calculated from data of Stanton is about 1.0, from data of Clement and Garland about 1.0, but from the work of Frost and Manley[55] only 0.5 when the interchanger was constructed of standard mild steel pipe.

The above formula reduces to: $h = 400\frac{c\ u^{0.8}}{z}$ if the fluid is water. (Thermal conductivity of water $= 0.329$. Hydraulic radius correction

[54] *Bull. M. I. T.*, 57, No. 33, March, 1922, 4-5.
[55] *Chem. Eng. Thesis*, Mass. Inst. Tech., 1921.

is small.) Lewis, et al., suggest that the value 0.5 be used for "c" for the present.

The equations cannot be applied if the linear velocity of the fluid in the pipe is less than the highest value of the critical velocity. Apparatus for heat transfer should always be designed in such a manner that the flow will be turbulent. According to Lewis, the range of critical velocities for an oil having a viscosity fifty times that of water and a specific gravity of 0.9 and flowing in a pipe 2.07 inches in diameter is 3.2 to 9.7 feet per second.

Transfer of Heat: Condensing Vapor ⇄ Solid.

Heat Transfer in Apparatus for the condensation of vapors, or more particularly for the condensation of steam, has been the subject of many investigations. The problem is a complicated one because vapors contain small to large amounts of non-condensible gases, and further because the thickness of the film of liquid formed is variable. The thickness of the liquid film is determined not only by the inherent properties of the liquid and by the conditions, but also by the nature of the apparatus. If the tubes are vertical the thickness of the liquid film increases from the top to the bottom of the tube. Obviously the rate of transfer through horizontal and vertical tubes will be very different. The resistances to heat flow on the vapor side is less than that on the liquid side if no non-condensible gas is present, but if gas is present in the vapor the higher resistance will be on the vapor side of the tube wall.

I am of the opinion that it is not possible at the present time accurately to calculate the resistance to the flow of heat from a vapor to a metal surface. The following paragraphs review or make reference to the more important studies of this problem.

The first thorough investigations of the condensation of steam were made by Joule.[56] However, the temperatures of the metal walls were not determined and the phenomena on the steam side and on the water side cannot be discussed separately.

The work of G. A. Orrok[57] is important, although he has been concerned mainly with the design of steam condensers. Also he has determined over-all coefficients and not film coefficients. The recommended formula for calculating H is

$$H = \frac{325\ u^{0.6}}{\Theta_m^{\frac{1}{8}}}$$

In steam condenser practice "u" varies from 7 to 10 feet per second. The corresponding average value of H is about 800 B.t.u. per sq. ft.

[56] *Trans. Roy Soc.*, London, 1861. Also in Joule's "Collected Papers," Vol. 1, p. 502, "The Surface Condensation of Steam."

[57] *J. Am. Soc. Mech. Eng.*, 32 (1910), 1139; 34 (1912), 713; 38 (1916), 864; 39 (1917), 212. (A review of Orrok's work by Ennis.)

per hr. per 1° F. If the tube is foul the value of H may be less than 400. Values of 250 to 300 are common in design.

Orrok investigated the effect of air on surface condensation. He found that Croton water as supplied to New York City contained 4.3 volumes of air dissolved in every one hundred volumes of water, that in passing through an open feed-water heater this quantity was reduced to 0.93 volumes, and that water from the hot well (80° F.) contained only 0.27 volumes of dissolved gas. The air discharged (at ordinary temp. and pressure) by a dry vacuum pump connected to condensing units, of 5000 kw. to 20,000 kw. size, varied from 1 cu. ft. per minute under good conditions to 20 cu. ft. when an ordinary amount of leakage occurred, and to 50 cu. ft. when the leakage of air into the condenser was excessive. The effect of the steam-richness ratio [58] should be represented by the quantity squared rather than raised to the fifth power. Reference must be made to Orrok's papers for the details of his work.

Obviously, Orrok's formula does not take into account all the variables and could not be expected to be generally applicable. The transfer of heat from steam to metal depends on mean temperature difference between the steam and the metal wall, viscosity of the liquid (or its reciprocal, the fluidity), temperature at which condensation occurs (viscosity and conductivity of the liquid vary with temperature), thermal conductivity of the liquid, velocity of the vapor, vapor density, condition of the condensing surface, presence of non-condensible gases, and on design of the apparatus, particularly as regards position of the tubes.

Webster [59] investigated the condensation of steam in an apparatus consisting of a ⅞″ O.D. and ½″ I.D. horizontally placed copper tube jacketed concentrically with another tube 1¾″ I.D. The steam condensed in the annular space between the two tubes, and the cooling water flowed through the inside tube. Webster concluded that at constant steam pressure and velocity the rate of condensation depended on the temperature difference between steam and metal. Further, that at constant temperature difference the rate of condensation was a function of steam velocity and steam pressure. Increasing the velocity of the steam from 1000 feet per minute to 4000 feet per minute, when all other conditions were constant, increased the rate of heat transfer from 1600 to 2400 B.t.u. per sq. ft. per min. per 1° F. Similarly, increasing the density of the steam from 0.05 pounds to 0.20 pounds per cubic foot by increasing the pressure while other factors remained constant, increased the rate of heat transfer from 1600 to 2100 B.t.u. per min. per sq. ft. per 1° F. These results are not in accord with those of Callender and Nicholson [60] who had previously stated that heat flow from condensing steam to a metal surface was independent of velocity

[58] *J. Am. Soc. Mech. Eng.*, 32 (1910), 1162.
[59] *Trans. Inst. Eng. and Shipbuilders in Scotland*, 57 (1913), 58.
[60] *Proc. Inst. Civ. Eng.*, 1897-8, Part I.

and pressure. However, Webster's investigation was much more comprehensive than that of Callender and Nicholson.

The value of the film coefficient "h" can, according to Webster, be calculated from the expression

$$h = 60 (C_1 \rho^n + C_2 V) \Theta_m$$

in which C_1 is a variable coefficient, C_2 a constant, "n" a variable exponent, ρ the density of the steam in pounds per cubic foot, and V the velocity of the steam in feet per minute. The values of the factors are:

	Steam Density	
	0.05 to 0.10	about 0.2
n	0.33	0.20
C_1	54.0	41.0

$C_2 = 0.36$ when V is given in feet per second.

In connection with Webster's work reference should be made to the previously mentioned article by Porter [61] and the editorial [62] in *Engineering*.

The use of an annular condensation space, of conditions not met in condenser practice, and failure to measure the temperature gradient along the tube, makes it questionable whether Webster's deductions and formula are applicable to condenser practice in general.

The effect of air in steam has been reviewed by C. S. Robinson,[63] who bases his discussion mainly on the data of E. W. Kerr.[64]

The over-all coefficient H is related to the film coefficient on the steam-side and water-side of a tube, and to the coefficient of heat transfer through the metal, that is, to h_s, h_e and k_m respectively by the expression

$$\frac{1}{H} = \frac{1}{h_s} + \frac{1}{k_m} + \frac{1}{h_e}.$$

Kerr's data gives the value of H only. Robinson approximates the other values as follows. The film coefficient for transfer of heat from steam to a metal wall "is stated by various writers to lie between 2000 and 4000" B.t.u. per hr. per sq. ft. per 1° F. Robinson selects 3000 as a mean value. Further h_e is a function of the water velocity. But H is also a function of the water velocity so it may be stated as

[61] *Engineering*, 107 (1919), 125-26, 140-42.
[62] *Engineering*, 107 (1919), 145-6.
[63] *J. Ind. Eng. Chem.*, 12 (1920), 644-6.
[64] *Trans. A. S. M. E.*, 35 (1913), 731.

an approximation that $h_e = f(k)$, or according to Robinson $h_e = ck^{0.8}$. Values of k_m can be found in tables of physical constants. Then, using $H = 594$

$$\frac{1}{594} = \frac{1}{3000} + \frac{1}{53{,}000} + \frac{1}{C(594)^{0.8}}$$

Hence $c = 4.55$. From another similar calculation in which a slightly different value of H was used, $c = 4.35$. The mean value $c = 4.45$ was selected. Using this value of c and the data from a third evaporator test as given by Kerr,

$$\frac{1}{510} = \frac{1}{h_s} + \frac{1}{53{,}000} + \frac{1}{4.45(510)^{0.8}}$$

$$h_s = 2500$$

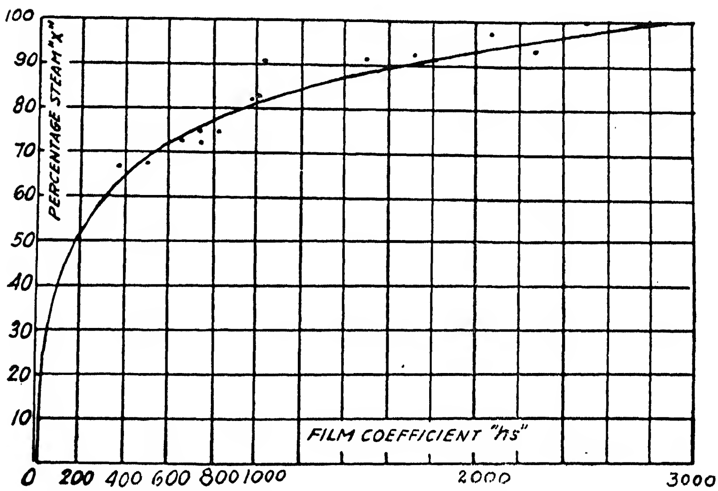


FIG. 31.—Effect of Air in Steam on the Film Coefficient "h_S."

The results of similar calculations of values of h_s are the basis of Figure 31 in which the film coefficient h_s is plotted against per cent of steam in steam-air mixtures.

The curve has the form represented by an exponential equation of the type

$$h_s = \alpha e^{\beta x}$$

in which α and β are constants to be determined and "x" the per cent steam by volume. The equation may be written in the logarithmic form

$$\log_e h_s = \log_e \alpha + \beta x.$$

This proves to be a straight line, and therefore when $x = 0$ $h = a$. The value of β was then calculated. The equation then may be reduced to the more convenient form

$$\log_{10} h_s = 1 + 0.0246\ x$$

which expresses the relationship between the per cent of steam and the film coefficient h_s.

A. F. Brewer and F. A. Stivers[64a] have studied four types of condensing equipment.

1. A 2-inch x 3-inch concentric double-pipe coil with water inside the 2-inch pipe. The fluid flow was countercurrent.
2. A 2-inch submerged coil with steam inside the coil.
3. A 2-inch coil manifolded into five sections and submerged as in (2).
4. A 2-inch coil manifolded into three equal vertical sections not submerged but cooled by water flowing downward. Flow of the fluids parallel.

The temperature of the cooling water was the same in all experiments. The quantity of cooling water, the quantity of steam, and the temperature of the condensate were varied independently. In all experiments the order of effectiveness was 1, 2, 3, 4. Coil number 4 was superior only if low cooling-water outlet temperature was desired. Tables of data are given.

W. H. McAdams and T. H. Frost[65] state that the film coefficient of heat transfer from condensing vapor to a metal surface is given by an expression of the form

$$h = b\ c_1\ k\ f\ u^n\ r_h^p$$

in which "b" is a constant of proportionality, c_1 a cleanliness coefficient, and "p" an exponent. All of the other symbols have the meaning given in the table of nomenclature. Their apparatus consisted of a standard 1½-inch steel pipe, through which a brass pipe 0.675 in. O.D. and 0.49 I.D. passed concentrically. The vapor condensed in the annular space between the pipes, and water flowed through the brass pipe in the same direction as the steam in the jacket. The axis of the tube was pitched 1-inch per foot. The values of "h" for the condensation of steam in this particular apparatus as shown by experiment varied from 2010 to 2650 B.t.u. per hr. per sq. ft. per 1° F. The average value was about 2400. These results are comparable to those of Clement and Garland who found values of 1470 to 2410 in a somewhat similar apparatus. Very limited experimentation with CCl_4 vapor and benzene vapor gave values of the film coefficient for these vapors of 280 and 340 respectively, or only about one-eighth the value for steam. It is interesting to note that if the coefficients for steam, CCl_4, and C_6H_6, are divided by the thermal conductivity and

[64a] *Mech. Eng.*, 43 (1921), 672-3.
[65] *J. Ind. Eng. Chem.*, 14 (1922), 13-18.

by the fluidity of the respective liquids the values obtained are 2240, 2500, and 1500 respectively. The eightfold difference becomes less than a twofold one. The authors mention that their communication is a preliminary one, and that further work is being done. It should be noted that they have taken no account of the effect of vapor density, presence of non-condensible gas, nor of the position of the tube. In another publication, Lewis, McAdams and Frost [66] give the following tentative equation from which the coefficient of heat transfer from a condensing to a metal surface may be calculated:

$$h = 2200 \frac{k}{z}.$$

Further work is in progress in their laboratory to determine the effect of vapor velocity and hydraulic radius. The value of "k" for water is given as 0.329, and the above equation applied to the condensation of steam becomes

$$h = \frac{725}{z}$$

In the article first cited, attention is also called to H. F. Weber's [66a] empirical relationship between the thermal conductivity of liquids and the specific heat and specific gravity. If the thermal conductivity "k" is divided by the density "s" and by the specific heat of the liquid "C," the product "a" varies from 0.182 to 0.329. But if "a" is multiplied by the cube root of the ratio of the molecular weight to the specific gravity of the liquid $\sqrt[3]{\frac{M}{s}}$ the product "a_2" varies only from 0.84 to 0.94. Weber's equation states that

$$k = \frac{a_2 C s}{\sqrt[3]{\frac{M}{s}}} = 0.868 \, C s \sqrt[3]{\frac{s}{M}}$$

Table XXXII gives a limited number of thermal conductivity data together with the calculated values of the several quantities mentioned. The value of the thermal conductivity of water calculated from this equation is 0.322 B.t.u. per hr. per sq. ft. per 1° F. per foot of thickness. This checks fairly well with Weber's observed value 0.329. The equation indicates that thermal conductivity should vary with temperature since both specific gravity and specific heat vary with temperature. However, the variation is a compensating one, for densities decrease and specific heats increase as temperature increases.

[66] *Bull. Mass. Inst. Tech.*, 57, No. 33, March, 1922, 6.
[66a] *Berl. akad.*, Ber., 1885, 809; and *Exners Reppert*, 22 (1886), 116. *Wied Ann.*, 48 (1893), 173.

TABLE XXXII

THERMAL CONDUCTIVITY OF LIQUIDS

Substance	Observer	Thermal Conductivity k	Sp. Gr. s	Sp. Ht. C_p	Mol. Wt. M.	$\sqrt[3]{\frac{M}{s}}$	$\frac{k}{sC_p} = a$	$\frac{k}{sC_p} \times \sqrt[3]{\frac{M}{s}}$
Methanol	Weber	0.12	0.81	0.586	32	3.41	0.263	0.895
Ethyl alcohol	Weber	0.1025	0.804	0.579	46	3.86	0.221	0.853
Propyl alcohol	Weber	0.0902	0.819	0.518	60	4.18	0.213	0.891
Chlorobenzene	Weber	0.0731	1.111	0.352	112.5	4.65	0.187	0.871
Carbon tetrachloride .	Weber	0.0610	1.63	0.205	153.8	4.56	0.182	0.840
Benzene	Weber	0.0806	0.873	0.460	78.0	4.48	0.201	0.900
Aniline	Weber	0.0990	1.039	0.497	93	4.47	0.192	0.857
Toluene	Weber	0.0742	0.884	0.440	92	4.71	0.191	0.896
Carbon disulphide	Graetz	0.0647	1.263	0.240	76.1	3.93	0.215	0.840
Chloroform	Weber	0.0697	1.503	0.234	119.4	4.31	0.198	0.855
Water	Weber	0.329	1.000	1.006	18	2.62	0.329	0.861
Glycerol	Weber	0.155	1.26	0.576	92	4.18	0.214	0.893
Acetic acid	Weber	0.1141	1.069	0.487	60	3.83	0.220	0.842
Average	......	......	.....	.....	.....	....	0.217	0.868

All data are for room temperature; source Landolt-Börnstein "Tabellen," 1912 ed. Compiled by W. H. McAdams and T. H. Frost.

Nusselt [67] and Parr [68] have formulated theories of surface condensation. These have been reviewed and briefly compared by Max Jacob.[69]

Jacob calls attention to the fact that both Parr and Nusselt used old values for the thermal conductivity of water. Jacob's [70] recent determinations at the Reichsanstalt cover the temperature range 0° C. to 80° C. are the most accurate available. The thermal conductivity of water is given by the expression

$$\lambda = 0.4769(1 + 0.00298\ t)$$

The result is obtained in kilogram calories per square meter per hour per 1° C. per meter.

Transfer of Heat: Solid ⟶ Boiling Liquid.

The transfer of heat from a solid to a boiling liquid is a complex phenomenon. No work of consequence has been done to determine film coefficients, nor has any systematic discussion of over-all coefficients been published. The data and conclusions of E. W. Kerr [70a] are, in my opinion, open to confirmation, since the former are unsystematic and the latter apparently unwarranted. Hausbrand's [71] discussion is not backed up by experimental data, although the manner of presentation is interesting and instructive. A recent article [72] by H. Classen gives a few data obtained in experiments with small apparatus. The discussion is qualitative in nature. Several other references are given below.

A start in the right direction has been made by W. L. Badger [73] and his collaborators, who have published four papers on the general subject, "Studies in Evaporator Design." The effect of temperature difference, of temperature at which heat transmission occurs, and of hydrostatic head has been studied. Professor Badger's papers are commended to the reader as the only thoroughgoing literature now available on this complex subject.

The Calculation of Over-all Coefficients from Film Coefficients and Metal Conductivity.

The total resistance to heat flow "R" is the summation of the separate resistances r_1, r_2, r_3, etc. The over-all coefficient of heat

[67] *Zeit. Ver. Deut. Ing.*, 60 (1916), 541-6, 569-75.
[68] *The Engineer*, 131 (1921), 559-60.
[69] *Zeit. Ver. Deut. Ing.*, 65 (1921), 1245-6.
[70] *Ann. Phy.*, 63 (4) (1920), 537. *Sitz. Akad. Wiss.* (1920), 406.
[70a] *Bull. No. 149*, Louisiana Agr. Exp. Sta. (1914).
[71] "Verdampfen, Kondensieren, und Kühlen," 7th Ed.
[72] *Z. Angew. Chem.*, 32 (1) (1919), 241-46.
[73] *Chem. Met. Eng.*, 23 (1920), 159-64, 237-4, 281-84, 390-93, 569-74. *Trans. Am. Inst. Chem. Eng.*, 13 (1920), Part I, 101-39, Part II, 139.

conductance H equals the reciprocal of R, and each component resistance equals the reciprocal of a coefficient of conductance "h". That is

$$H = \frac{1}{R} = \frac{1}{r_1 + r_2 + r_3} = \frac{1}{\frac{1}{h_1} + \frac{1}{h_2} + \frac{1}{h_3}}$$

The conductance of unit area of the metal wall may of course be calculated from the thermal conductivity of the metal.

$$h_2 = \frac{\text{conductivity}}{\text{thickness}}$$

The total heat transferred is given by the expression:

$$Q = H\,A\,\Theta_m$$

Chapter VI.

Refinery Equipment for Distilling Petroleum.

The separation of several fractions from crude oil may be conducted either as a batch distillation or as a continuous process. The first of these is the older and is still a common method. The apparatus is known as a fire-still, and consists of a cylindrical steel tank supported by means of cast-iron or steel lugs that rest on cast-iron columns or structural steel supports. Fire-stills of 150 to 1200 barrel charging capacity are used. The actual volume of the 1200 barrel still is between 1400 and 1500 barrels, which means that the diameter is about 16 feet and the length 40 feet. The upper portion of a still is made of ⅜-inch to ½-inch steel plates, and the bottom of a single ¾-inch or 1-inch plate. Though the bottom should be a continuous sheet, in order to avoid exposure of a riveted seam to the hot flue gases, it is not always possible to obtain so heavy a plate in so large a size. In this event two bottom plates are used. The end plates of the still are stiffened by riveting on several angle irons, or by "bumping" the head. The still is provided with two or more manhead openings along the top, and one on one end. The latter should be of ample dimension to facilitate the removal of coke. A dome with a baffle may be provided. If so, the vapor line is connected to the top or to the side of the dome. Provision is made for connecting the charging line, draw-off line, steam line, vacuum and pressure relief valves, and any other lines that special circumstance may require. The steel flange connection for the draw-off line should be placed at the end of the bottom plate, away from the fire, and should be protected with brick work and insulation. Inside the still is a special seat for the "tar-plug." The plug is connected by a rod that passes through a stuffing box atop the still to a means for quickly dropping the rod and plug in case of a break in the line through which the hot residuum is drawn off at the completion of a distillation. If the charge in the still is to be coked, the plug is closed before the still is charged to prevent the oil from filling the draw-off pipe and becoming coked therein. Figure 32 shows a still ready for shipment to the oil-refiner. The design of the still-setting depends on whether the still is to be fired with coal, oil or gas. In general a substantial reinforced concrete foundation is laid, and the brickwork built upon this.

The concrete foundation should not consist of a pad, but rather of beam footings upon which the brickwork may be built. The amor-

phous hydrated aluminates and silicates that compose the cementing material in a concrete are seriously affected by heat as a result of dehydration. For this reason, as well as on account of volume change, the concrete work of a setting must never be exposed to high temperatures. The papers of White [1] and of Abrams [2] should be consulted on the mixture and use of concretes. Mills [3] summarizes the investigations on the constitution and use of Portland Cement.

The setting is made of red brick lined ordinarily with but a 4½-inch course of fire brick. A 2½-inch course of insulating brick or other type of insulating layer may be used with profit. The whole setting should be held together with buck-stays and adjustable tie-rods.

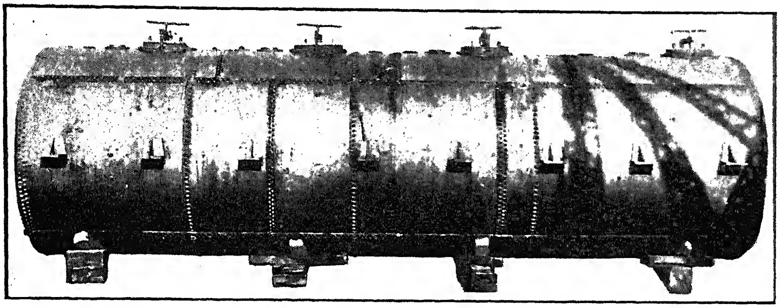


FIG. 32.—Fire-Still Ready for Shipment.

The exposed surfaces of the still should always be carefully insulated to avoid heat loss and to prevent excessive decomposition of the heavy oil that will occur if it condenses on the still-wall and drops back into the hot oil. The insulation should be readily removable since fire-stills, when used for batch distillations, are prone to develop leaks at the seams as a result of stresses caused by sudden temperature change when the still is charged. The use of one type of insulating material on the still surfaces and in the setting is shown in Figure 33.

Insulating material that will not absorb oil or vapor is desirable since oil increases the heat conductivity of the material, and also unnecessarily spreads the fire if the vapor or oil is ignited. A novel still-insulation [4] is made of a sheet metal box 3′-0″ by 3′-0″ thick and of such curvature that it can be fitted to the still. The box is filled with heat-insulating material. This type of insulation will stand the wear and tear of service, and also possesses a salvage value.

Interesting booklets containing valuable technical information have been published by the Armstrong Cork and Insulation Company and

[1] *Trans. Int. Eng. Cong.*, 1915, 242.
[2] *Proc. Am. Soc. Test. Mat.*, 20 (1920), Pt. I, 437-440.
[3] "Materials of Construction," Revised 1921.
[4] See Staff Special, *Nat. Pet. News*, Nov. 9, 1921, 29-30.

by the Celite Products Company. Saving of 60 to 65 per cent of the heat wasted is claimed.

The vapor formed in the still passes through a 12-inch to 16-inch line to the towers, or in the simplest form of equipment, directly to the condenser. The vapor-line is sometimes inclined and made to serve as an aerial-reflux from which the condensate runs back to the still. The subject of towers or fractionating condensers and of water-condensers is discussed in Chapter VII.

Figure 34 shows a battery of fire-stills of the simplest form. The stack for the battery is seen at the left of the picture.

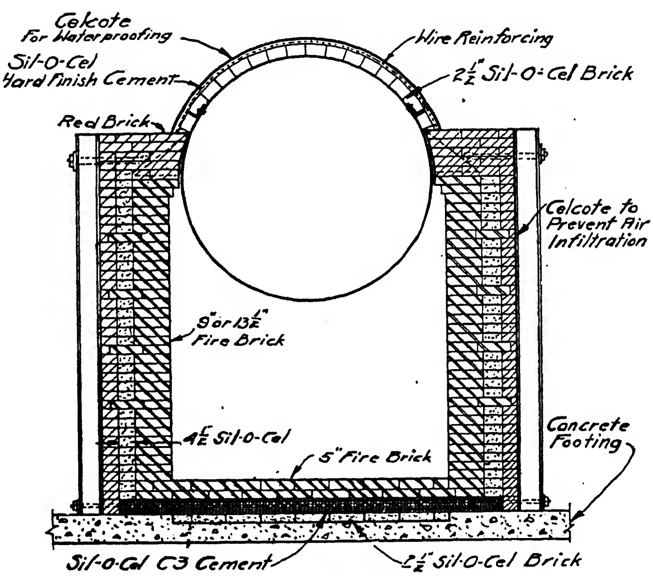


FIG. 33.—Insulation of Still and Setting.

Figure 35 shows a sectional longitudinal-elevation and Figure 36 a sectional end-elevation of a battery of four conventional crude-stills. Each still is 10 feet in diameter and 40 feet long and of 600 barrel capacity. One end of the still is supported 6 inches above the other end to facilitate complete removal of residuum. Steel plates are placed beneath the cast-steel supporting-lugs in order to provide opportunity for slip when expansion or contraction occurs. Baffle walls are ... in the combustion chamber beneath the stills in order to direct ...e-gases against the still-bottom. The exposed portion of the ... covered with sheet asbestos on which curved tiles are laid and ...ed in place. Gutters provide means for removal of rain-water.

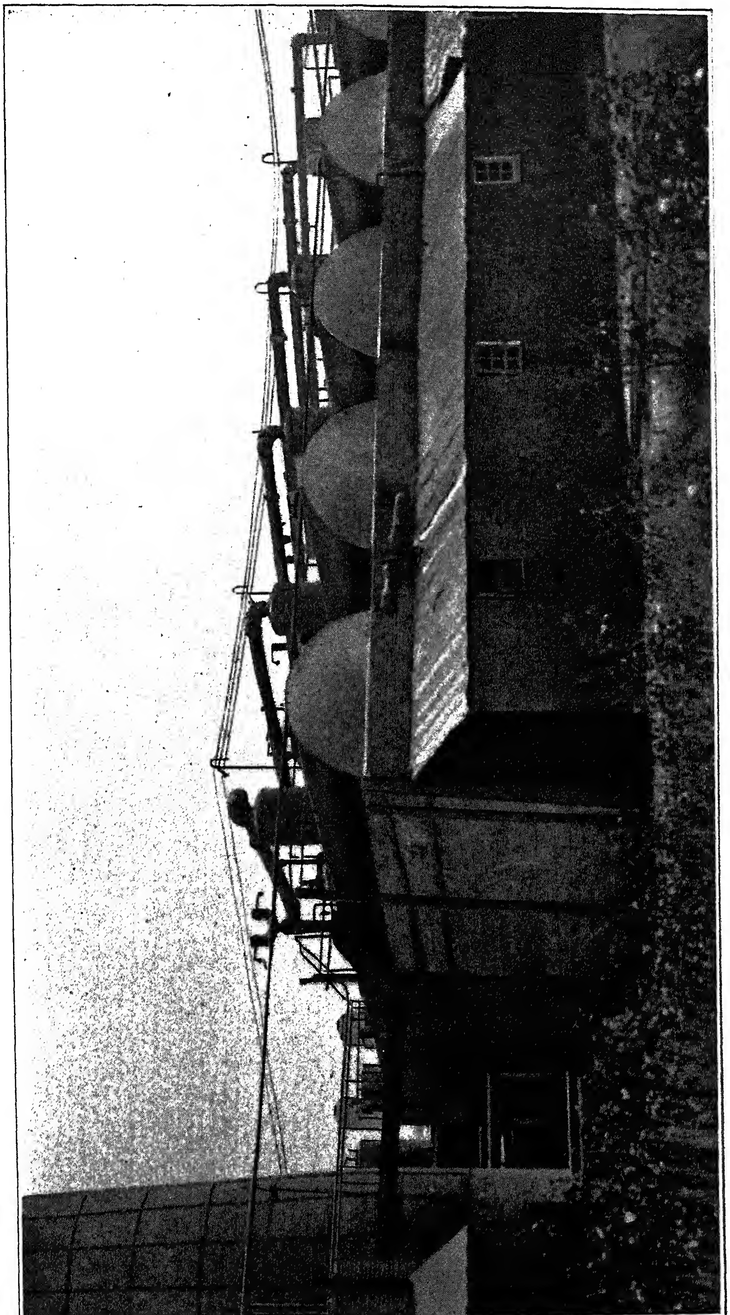


Fig. 34.—Battery of Fire-Stills.

TABLE XXXIII

OPERATING DATA OF CONTINUOUS-STILL PLANT AT AVON, CAL.[6]

Gravity of crude run		Temperature of in-going crude		Still 1				Still 2				Still 3				Still 4				Residuum			
				Temperature of vapors		Gravity of distillate		Temperature of vapors		Gravity of distillate		Temperature of vapors		Gravity of distillate		Temperature of vapors		Gravity of distillate		Gravity		Flash point[a]	
° B.	Specific gravity	° F.	° C.	° F.	° C.	° B.	Specific gravity	° F.	° C.	° B.	Specific gravity	° F.	° C.	° B.	Specific gravity	° C.	° F.	° B.	Specific gravity	° B.	Specific gravity	° F.	° C.
26.6	0.8945	265	129.40	290	143.3	58.3	0.7435	340	171.1	52.6	0.7667	386	196.65	47.5	0.7887	415	212.7	43.0	0.809	20.4	0.931	158	70.0
26.7	.8935	250	121.0	290	143.3	....	......	340	171.1	56.5	.7507	390	198.9	47.3	.7896	415	212.7	43.7	.806	20.4	.931	159	70.55
25.6	.900	260	126.7	287	141.65	58.3	.7435	340	171.1	52.5	.767	390	198.9	47.0	.7910	415	212.7	43.5	.807	20.0	.933	144	62.20
26.7	.8935	250	121.0	285	140.55	58.5	.7427	340	171.1	53.0	.765	387	197.4	47.5	.7887	415	212.7	43.8	.8055	20.4	.931	170	76.65
25.6	.900	250	121.0	290	143.3	58.3	.7435	340	171.1	52.4	.7675	390	198.9	47.7	.7878	415	212.7	43.6	.8065	20.0	.933	156	68.85

[a] Open cup tester.

[6] *U. S. Bur. Min. Bull. No. 162*, 7.

The Continuous Distillation of Petroleum.

In recent years the use of methods of continuous distillation of petroleum has become a common practice in the larger refineries. The operating advantages of this procedure lie in the smaller labor and fuel costs for a unit through-put of oil, and in the smaller initial investment for a given capacity. Conditions may be adjusted with greater nicety.

Apparatus for continuous distillation can be designed with greater exactness than that for batch-distillation. This is especially true when the material to be distilled is, within reasonable limits, of uniform composition. Flexibility as to nature of products is easy of attainment in properly designed equipment, altho not so easy as might be desired in some continuous apparatus that has been built.

Distillation equipment now in general use in the petroleum industry can hardly be said to be better than crude. The engineering often is excellent in the sense that good materials are used and layout carefully considered. But the fundamental physics and thermodynamics, of which physical structures should be the expression, are sadly neglected. The result is unnecessary expenditure of money both for equipment and operation, and sacrifice of flexibility and ease of operation. I regret, on account of patent matters, that I shall not be able to go into as much detail in this connection as I should like. However, in Chapter VII I shall critically discuss the apparatus used in the Trumble process in an effort to show what I mean by the foregoing statements. Comparison of batch and continuous distillation methods will be made after the continuous systems have been described. In general two types of continuous plants are used; (1) the battery of several stills, (2) the pipe-still plant.

Batteries of Stills for Continuous Distillation.

The battery of four 600 barrel stills shown in Figures 35 and 36 is operated as a continuous unit.[5] The crude oil passes through a cylindrical tank of 300 barrel capacity, where, as a result of lowered velocity, some water settles out. The oil is then forced by means of two 8 x 8½ x 10 duplex-pumps through a heat-exchanger. The hot outgoing residuum is passed through the exchanger counter-current to the incoming oil. The oil at a temperature of 260° F. enters the rear of the first still, and then flows through each of the other stills. The temperature increases from still to still, and in the last still "bottom-steam" is used. Table XXXIII shows the operating data for two still-batteries of this type when running a California oil of 0.897 sp. gr. or 26° Bé. The daily capacity was 6,696 barrels when the temperature of the vapor from the last still was 400 to 450° F. Approximately 25 per cent of the oil was vaporized under these conditions. Table XXXIV shows boiling range of the distillates from each still.

The volume of fuel consumed was 1.1 per cent of the volume of

[5] See p. 6 of *U. S. Bur. Min. Bull. No. 162.*

TABLE XXXIV

Results of Engler Distillations of Condensate from Each Vapor-Line in Crude-Still Battery No. 2 at Avon Refinery, Jan. 29, 1916

Still 1 condensate, gravity 58.7° Bé. (specific gravity, 0.742)

Boiling Point °F.	Boiling Point °C.	Per Cent Over
100 to 167...	37.8 to 75 ..	11.5
167 to 212...	75 to 100 ..	29.5
212 to 250...	100 to 121.2 ..	26.5
250 to 300...	121.2 to 148.8 ..	18.5
300 to 350...	148.8 to 176.65..	8.5
350 to 400...	176.65 to 204.40..	2.5
Bottoms	....	2.1
Total	....	99.1

Still 2 condensate, gravity 52.5° Bé. (Specific gravity, 0.767)

Boiling Point °F.	Boiling Point °C.	Per Cent Over
149 to 167...	65 to 75 ..	1.5
167 to 212...	75 to 100 ..	15.0
212 to 250...	100 to 121.2 ..	32.0
250 to 300...	121.2 to 148.8 ..	24.5
300 to 350...	148.8 to 176.65..	14.5
350 to 400...	176.65 to 204.40..	6.5
Bottoms	....	5.9
Total	....	99.9

Still 3 condensate, gravity 47.1° Bé. (specific gravity, 0.7905)

Boiling Point °F.	Boiling Point °C.	Per Cent Over
198 to 212...	92.2 to 100 ..	1.0
212 to 250...	100 to 121.2 ..	18.5
250 to 300...	121.2 to 148.8 ..	30.0
300 to 350...	148.8 to 176.65..	23.0
350 to 400...	176.65 to 204.40..	13.5
Bottoms	....	14.0
Total	....	100.0

Still 4 condensate, gravity 42.9° Bé. (specific gravity, 0.8095)

Boiling Point °F.	Boiling Point °C.	Per Cent Over
230 to 250...	110 to 121.2 ..	4.5
250 to 300...	121.2 to 148.8 ..	23.0
300 to 350...	148.8 to 176.65..	25.5
350 to 400...	176.65 to 204.4 ..	20.0
Bottoms	....	27.0
Total	....	100.0

TABLE XXXV

Detailed Costs of Two Batteries of Topping Stills

(Based on Prices of 1912)

	Excavation	Concrete	Brick-work	Iron-work	Unit	Pumps	Pipe Covering	Piping	Total
8 Stills	$1,800	$5,000	$13,000	$9,500	$18,000	$1,055	$100	$6,744	$55,199
8 Condensers ..	632	5,104	......	2,224	9,199	......	....	13,903	31,062
2 Heat Exchangers	......	500	......	904	......	......	....	6,120	7,524
1 Residuum Cooler	.....	.....	......	.....	......	.....	....	750	750
Tail House, 3 Look Boxes...	49	664	......	262	2,000	......	....	5,120	8,095
Oil-Pump Plant[a]	400	1,322	......	1,025	5,000	16,096	75	2,700	18,100
Salt-Water Plant[a]	99	575	......	114	375	2,550	....	375	2,780
Boiler Plant[a] ..	480	1,718	3,272	1,636	16,955	9,718	428	3,300	25,505
Total.........	3,460	14,883	16,272	15,665	51,529	29,419	603	39,012	149,015

[a] Only that proportion chargeable to these two still batteries is included.

crude oil distilled. The consumption of steam was not known exactly. The distillates from the topping stills were re-run in four combination steam- and fire-stills and in two steam-stills. Salt water was supplied to the condenser boxes by two 8-inch centrifugal pumps connected directly to two 50 H.P. motors. The water required varied with temperature and humidity, but averaged 14 barrels of water for each barrel of distillate. The cost of the labor and supervision chargeable against the operation of the continuous topping-stills was $52.50. The first cost of the stills is given in Table XXXV.

A part of the cost of the re-running plant that served the entire refinery is properly chargeable to the topping plant. If this is included the total cost of the topping equipment was $224,945 or about $16.80 per barrel of daily topping capacity. As will be seen this is much higher than the unit cost of continuous distillation equipment of other types.

The efficiency of this battery of topping stills has been calculated by Wadsworth.[6] The analysis of the fuel oil was

	Per cent
Carbon	85.6
Hydrogen	11.9
Oxygen	0.9
Nitrogen	0.5
Sulphur	1.1

Calorific value 18,640 B.t.u. per pound.

The theoretical fuel consumption for removing a 25 per cent cut by volume from 1 pound of oil as fractionated is as follows:[6a]

Assume:

1. No heat lost from the stills.
2. Heat recovery in the exchangers sufficient to raise the temperature of the oil entering Still No. 1 to 250° F.
3. Mean specific heat of oil 0.45 B.t.u. per 1° F.
4. Latent Heat of Evaporation of the distillate 125 B.t.u. per pound.
5. Specific heat of the vapors 0.50 B.t.u. per 1° F.

Then:

		B.t.u.
Heat 0.938 pound of oil 250-300° F. (121.1-148.8° C.)	0.938 (250-300° F.) × 0.45	= 21.12
Evaporate 0.058 pound of vapors	.058 × 125	= 7.25
Heat 0.879 pound of oil 300-350° F.	.879 (300-350° F.) × .45	= 19.80
Evaporate 0.0346 pound of vapors	.0346 × 125	= 4.33
Heat 0.845 pound of oil 350-400° F.	.845 (350-400° F.) × .45	= 19.00
Evaporate 0.024 pound of vapors	.024 × 125	= 3.00
Heat 0.820 pound of oil 400-450° F.	.820 (400-450° F.) × .45	= 18.45
Evaporate 0.030 pound of vapors	.030 × 125	= 3.75
		96.70

Heat consumed per pound of oil topped at 100 per cent efficiency = 96.70 B.t.u., or 24.40 calories.

[6] *U. S. Bur. Min. Bull. No. 162*, 11-13.

[6a] Calculated by Wadsworth, *Bull. No. 162*, U. S. Bur. of Min.

One barrel of 26° Bé. (sp. gr. 0.8974) oil weighs 314.4 pounds. The theoretical heat required to remove a 25 per cent cut by volume is 96.7 B.t.u. $\times$ 314.4 = 30,402.5 B.t.u. The actual requirement was 68,325 B.t.u. from fuel oil burned plus 19,250 B.t.u. in the form of steam, or a total of 87,575 B.t.u. Hence

$$\text{Over-all Efficiency of the battery of stills} = \frac{30,402}{87,575} \times 100 = 34.8 \text{ per cent.}$$

The distillation of the crude oil is shown in Table XXXVI.

TABLE XXXVI
DISTILLATION OF CRUDE OIL (25.6° Bé.)

Boiling point		Specific gravity of fraction	Percentage of crude evaporating		Specific gravity of fraction	Residue remaining	
° F.	° C.		By volume	By weight		By volume	By weight
160 to 212	71 to 100	0.700	2.5	1.94	0.906	97.5	98.06
212 to 250	100 to 121.1	.720	5.25	4.26	.917	92.25	93.80
250 to 300	121.1 to 148.8	.742	7.00	5.84	.918	85.25	87.96
300 to 350	148.8 to 176.65	.767	4.00	3.46	.923	81.25	84.50
350 to 400	176.65 to 204.4	.790	2.75	2.45	.925	78.50	82.05
400 to 450	204.4 to 232.2	.806	3.38	3.07	.932	75.12	78.98

Data covering a number of tests of efficiency of the furnaces under these stills are contained in Tables XXXVII and XXXVIII.

TABLE XXXVII
COMBUSTION DATA, FIRE-STILLS

Apparatus	Number of test	Flue-gas analyses								Air required per pound of fuel	Air used per pound of fuel	Per cent of excess air	Weight of flue gas per pound of fuel
		Per cent by volume				Per cent by weight							
		CO_2	O	CO	N	CO_2	O	CO	N				
										Pounds	*Pounds*		*Pounds*
Crude stills	1	5.8	13.8	....	80.4	8.63	15.0	....	76.4	13.96	36.88	165	36.76
Do	2	5.2	13.4	....	81.4	7.8	14.6	....	78.0	.....	40.56	191	39.41
Do	3	7.3	12.4	....	80.3	10.8	13.4	....	75.6	.....	28.60	104	28.76

These data show that there was much room for improvement in the design and operation of these furnaces. A very common carelessness in the operation of stills is the admission of a large excess of air to the combustion chamber.

The performance of the heat exchanger is shown in Tables XXXIX and XL. These exchangers consisted of four rows each of five 9-inch casings, 48 feet long, laid parallel, and connected by special castings to form a continuous coil. Within the 9-inch casing were five sets of 2-inch continuous pipe coils.

TABLE XXXVIII

FURNACE AND STACK TEMPERATURES, WITH HEAT LOSSES AND FURNACE EFFICIENCIES, FIRE-STILLS

Apparatus	Number of test	Atmospheric temperature		Stack draft	Observed furnace temperature	Stack temperature		Weight of gases per pound of fuel	Computed temperature of products of combustion	
		° *F.*	° *C.*	*Inches of water*		° *F.*	° *C.*	*Pounds*	° *F.*	° *C.*
Crude stills ...	1	58	14.4	.....	.....	665	351.6	36.76	2,023	1,106.1
Do	2	60	15.55	0.70	.....	650	343.3	39.41	1,892	1,033.3
Do	3	60	15.55	.62	.....	650	343.3	28.76	2,592	1,422.2

Apparatus	Number of test	Heat loss from excess air		Fuel loss	Furnace efficiency	Remarks
		B.t.u.	*Calories*	*Per cent*	*Per cent*	
Crude stills ...	1	3,477	875	18.6	38.0	Normal operation.
Do	2	3,918	986	21.0	34.6	Dampers one-fifth open.
Do	3	2,159	544	11.6	48.5	Dampers one-seventh open.

TABLE XXXIX

AVERAGE RESIDUUM TEMPERATURES IN THE HEAT EXCHANGERS OF CRUDE STILLS DURING NOVEMBER, 1916

Average number of barrels of residuum each hour	Average gravity of each barrel		Average weight of each barrel	Temperature of residuum				Heating surface	θ_m	
				Ingoing		Outgoing				
	° Bé.	Specific gravity		° F.	° C.	° F.	° C.	Square feet	° F.	° C.
			Pounds							
197.97	18	0.946	331.2	404.2	206.75	149.4	65.20	2,889.21	98.3	36.8

TABLE XL

AVERAGE CRUDE-OIL TEMPERATURES IN THE HEAT EXCHANGERS OF THE CRUDE-STILLS DURING NOVEMBER, 1916

Average number of barrels of crude oil each hour	Average gravity of each barrel		Average weight of each barrel in pounds	Temperature of Crude				Heat transmitted per sq. ft. per hour per degree of mean temperature difference (K)	Heat apparently transmitted per sq. ft. per hour per degree of mean temperature difference (K_1)
				Ingoing		Outgoing			
	° Bé.	Sp. gr.		° F.	° C.	° F.	° C.		
268.98	26	0.8974	314.0	87.4	30.75	258.6	125.85	22.8 B. t. u.	23.8 B.t.u.

Figures 35 and 36 show the stills, vapor lines and condensers of the continuous battery just described. The heat-exchangers are beneath the condensers.

The data covering the operation of these continuously operated batteries of stills are of interest and value, but are not to be regarded as ideal in any sense. Obviously the design of the combustion chamber could be improved. The air for combustion should be preheated and far more carefully controlled in amount. The stills should be fitted with efficient fractionating equipment to avoid the necessity of a second

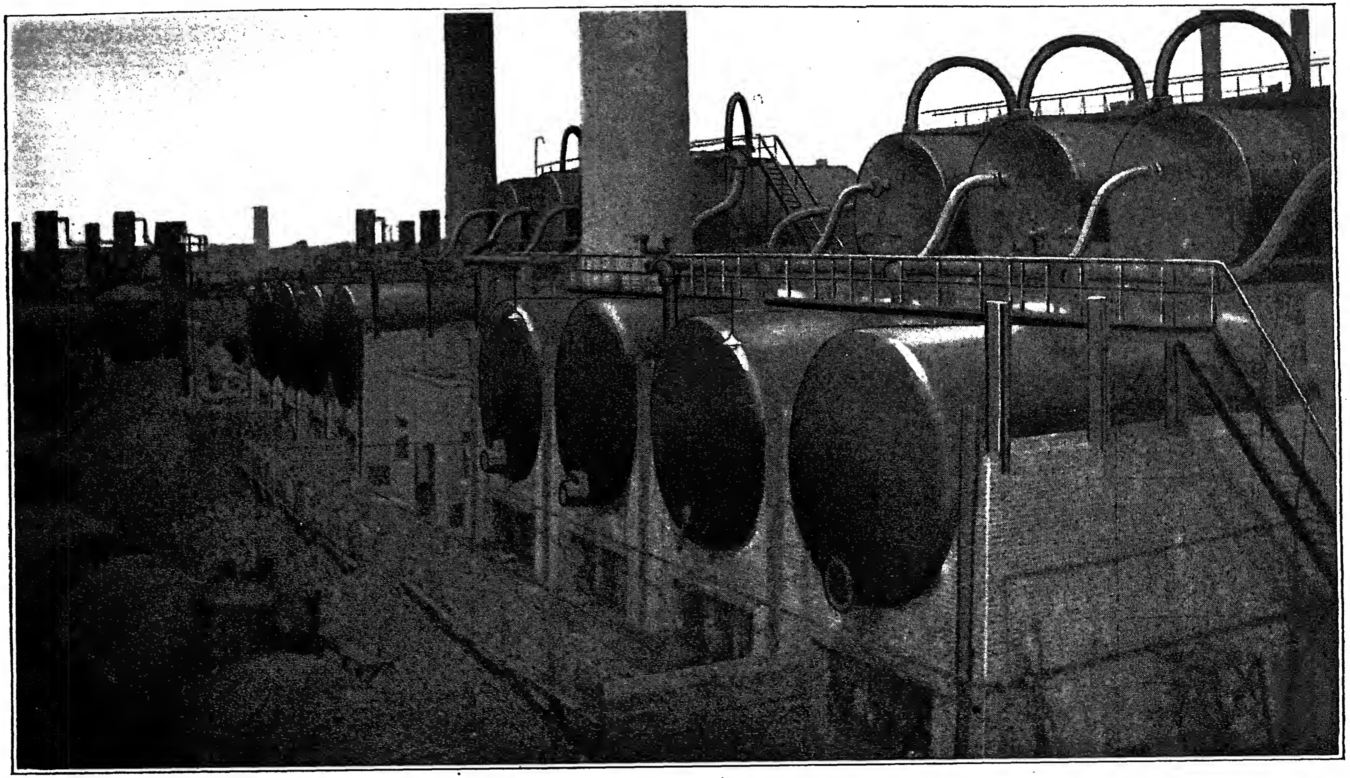


Fig. 37.—Battery of Continuous Stills at the Plant of the Paragon Refining Company.

distillation. The design of the heat exchangers is such that the velocity of the fluids is fairly high, and the coefficient of heat transfer is high as compared to the coefficients shown by many apparatus used in refineries, but low as compared to the coefficients obtained (200 to 400) with less viscous fluids.

Figure 37 shows two batteries of continuous stills, the layout of which is such as to effect a better heat economy than the battery just described. The crude oil is pumped through an interchanger countercurrent to the outgoing 18 to 20° Bé. residuum. It then passes to the upper stills, which operate in parallel, and which are heated by coils through which the hot vapors from the lower stills are passed. The vapors from the upper stills are combined and condensed. The hot oil from the upper stills flows through the lower stills in series. The vapor from each lower still passes to the corresponding upper still where it is partially condensed. The uncondensed vapor passes to a water-condenser. The residuum from the last lower still passes through the heat exchangers. This battery of stills in some respects resembles continuous batteries formerly used in Russia.

The plant of the Union Oil Company of California, located at Avila, California, and designed by E. I. Dyer uses high and low pressure stills operated in double effect. The process is economical, and is admirably suited to the treatment of oils containing 10 to 15 per cent of salty water. The details of this process are given by A. F. L. Bell,[7] and by J. M. Wadsworth.[8]

Batteries of stills so arranged as to operate continuously and to conserve heat are surely superior to that crudest of all possible distillation equipment, the batch fire still. In some circumstances the continuous-still battery is to be preferred to the pipe-still. Yet in my opinion the use of a conglomeration of stills, however cleverly designed and arranged, is in many instances nothing more than an expression of the technical limitations of the engineer. The desired results can be accomplished by the use of properly designed column apparatus at a less cost for both equipment and operation. The extensive use of the fire-still is convincing testimony of the tendency of the human mind to follow the line of least resistance—the rut of precedent.

Continuous Distillation with Pipe Stills.

The pipe-still topping plant is distinctly a California development that grew out of the necessity for a quick and cheap means for removing small quantities of light distillates from heavy crude oils. Among the more important plants in California are those built after the designs of M. J. Trumble, A. F. L. Bell, and I. W. Fuqua. Pipe-still distillation is now extensively used in Mexico.

The following discussion will be limited to a description of the Trumble plants of the General Petroleum Corporation and Shell Company of California and to the Lederer plant of the Atlantic Gulf Oil Company at Tecomate, State of Vera Cruz, Mexico.

[7] *U. S. Bur. Min. Bull. No. 162.*
[8] *Bull. Am. Inst. Min. Met. Eng.,* 1915, 1770-75.

The Trumble System of Distillation.[9]

The first really successful Trumble plant was built at Fellows, Kern County, California, for the Santa Fé R. R. Company. The products were "tops" and fuel oil.

A one-half interest in the Trumble patents was purchased by the General Petroleum Company, and a 12,000-barrel plant was erected in 1912 at Vernon, California, on the outskirts of Los Angeles. The cost of this plant was about $80,000.

In May, 1915, the Trumble patents were purchased by the Shell Company of California through a subsidiary company known as the Simplex Refining Co. The reported consideration was $1,000,000. The Shell Company erected two plants at Martinez, California.

The central idea of the Trumble system of distillation is the efficient use of heat in making clean-cut separations. To accomplish this an effort is made to utilize the heat content of vapors, residuum, and flue-gases. A process of fractional condensation rather than fractional distillation is used to make the rough-cuts. Those distillates of too broad distillation range are re-run in continuous steam stills called separators. In general, tubular heat exchangers and condensers are used.

A flow sheet of one of the units of the first plant built at Vernon, California, is shown in Figure 38.[10] The General Petroleum Corporation, as a result of the efforts of their refinery superintendent, Mr. Harry Isaacs, and the Shell Company as a result of the studies of their engineering department, have both improved on the design of this plant in many ways in plants recently built. However, to gain an idea of the general scheme of a Trumble plant this flow sheet serves very well. The incoming crude oil passes through tubular heat exchangers countercurrent to the hot outgoing residuum, and then enters the heating retorts. These were six 12½-inch pipes, 20 feet long, and connected outside the furnace by 4-inch return bends. Vent pipes were placed at one end of each retort to prevent accumulation of gas and overheating of part of the retort as a consequence. As may readily be imagined these retorts were found unsatisfactory. They proved to be an inefficient heating means, and also they sagged and carbonized. To increase the heating surface a supplementary set of 4-inch pipes was placed above the 12-inch pipes. The 50 per cent increase in heating surface was sufficient to cause a lowering of the [illegible] gas temperature from 1,200° F. to about 650° F.

[illegible] oil from the retorts passes upward and is discharged into

[9] For further details of the various Trumble plants see Bell, A. F. L., "Important Topping Plants of California," *Bull. Am. Inst. Min. Met. Eng.*, 1915, [illegible]. Thompson, N. W., "The Trumble Refining Process," *J. Am. Soc. Mech. Eng.*, 39 (1917), 831-4; *Met. Chem. Eng.*, 18 (1918), 256-7. Wadsworth, J. M., U. S. Bur. Min., *Bull. No. 162.* U. S. Patents: 996,736, July 5, 1911; 1,0[illegible]2,474, Sept. 5, 1911; 1,070,301, Aug. 12, 1913; 1,259,171, March 12, 1918; 1,260,598, March 26, 1918.

[10] From Bell's, A. F. L., article, 1791.

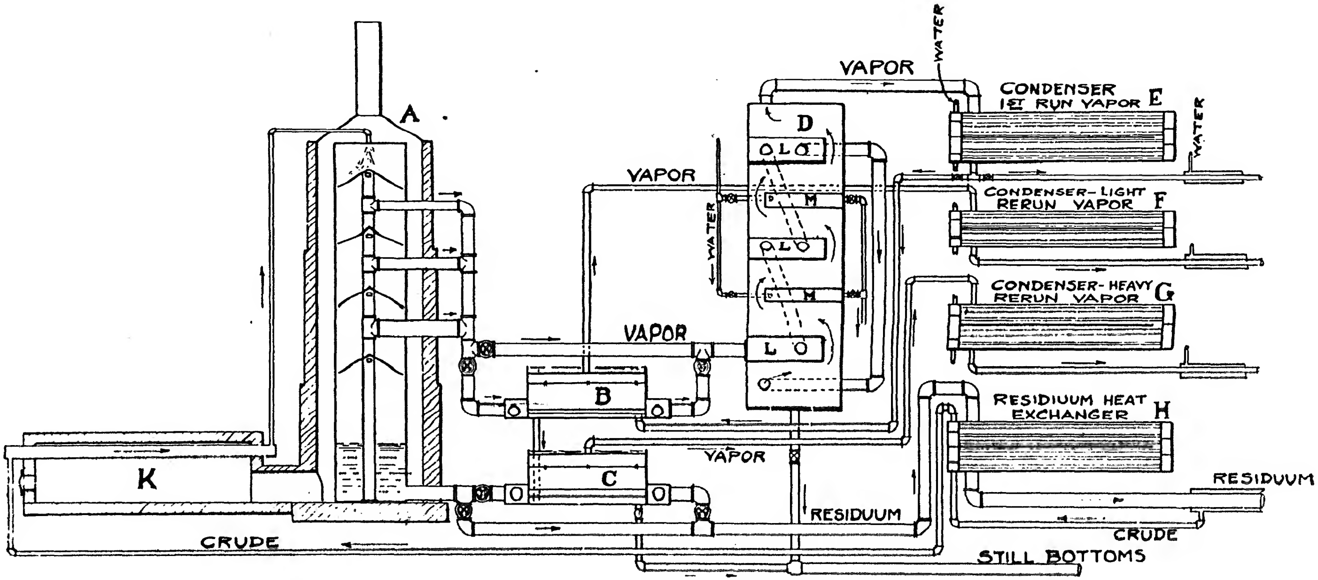


FIG. 38.—Diagram and Flow-Sheet of First Trumble Plant Built at Vernon, Calif.

the top of the evaporator onto the spreader-cones. The vapor is thus flashed from the oil. The proportion of the oil vaporized in this manner depends on the temperature to which the oil is heated. The less volatile portion of the oil is directed to the side walls of the evaporator. Further distillation occurs as the film flows downward. The hot residuum collects in the bottom of the evaporator where steam is blown through it from a perforated coil. A constant liquid level is maintained. From the evaporator, hot residuum flows through the heating tubes of one or more separators and thence through the heat-exchangers and coolers to storage.

The vapor is collected by the vertical pipe within the evaporator, led out and through the heating-tubes of a separator, passes through one or more dephlegmators or fractionating-condensers, and thence to tubular water-cooled condensers. A condensate is formed in each dephlegmator that may be re-run in a separator if desired. The distillate from the water-cooled condensers is re-run in continuous steam-stills called "separators." The vapor from each separator is condensed in tubular water-cooled condensers. All distillates pass through tubular or "jacketed-line" coolers on their way to storage. Very little gas is formed, since the tubular condensers serve as scrubbers so that the gas and lightest vapors are thoroughly washed by the distillate.

The later Trumble plants of the General Petroleum Corporation and of the Shell Company are of improved design in several respects. Figure 39 [11] is a simplified flow-sheet of the plant of the Shell Company at Martinez. The entering crude-oil passes counter-current to the out-going residuum, and is then discharged into an auxiliary evaporator called an "evaporator-column." The lighter hydrocarbons are here volatilized. The remaining oil is pumped from the bottom of the evaporator-column through the heating-coils of 4-inch pipe. The use of the smaller sized heating-pipe is a great improvement. The exchange of heat is far more rapid, the sagging and carbonization eliminated, and gas collection is impossible. The pressure in the heating-coils is less as a result of the removal of the very volatil hydrocarbons in the evaporator-column. The dephlegmators are not shown in Figure 39, nor are the small dephlegmators, placed in the vapor-line from the separators, shown. The vapors exiting from the separators were found to contain too wide a range of hydrocarbons. To remedy this the last mentioned dephlegmators were added.

The flow of the crude oil and residuum in the Shell Company's plant at Martinez is shown in Figure 40.[12] The crude oil is pumped to the plant through a 6-inch line and passes through the six coolers in parallel. The coolers are of tubular type, 30 inches in diameter, and containing 62 2-inch x 18-foot-0-inch tubes. The oil enters the bottom, flows through the tubes in four passes, and exits from the top of the cooler.

[11] From Bell's, A. F. L., article, 1795.
[12] From Thompson's, N. W., article.

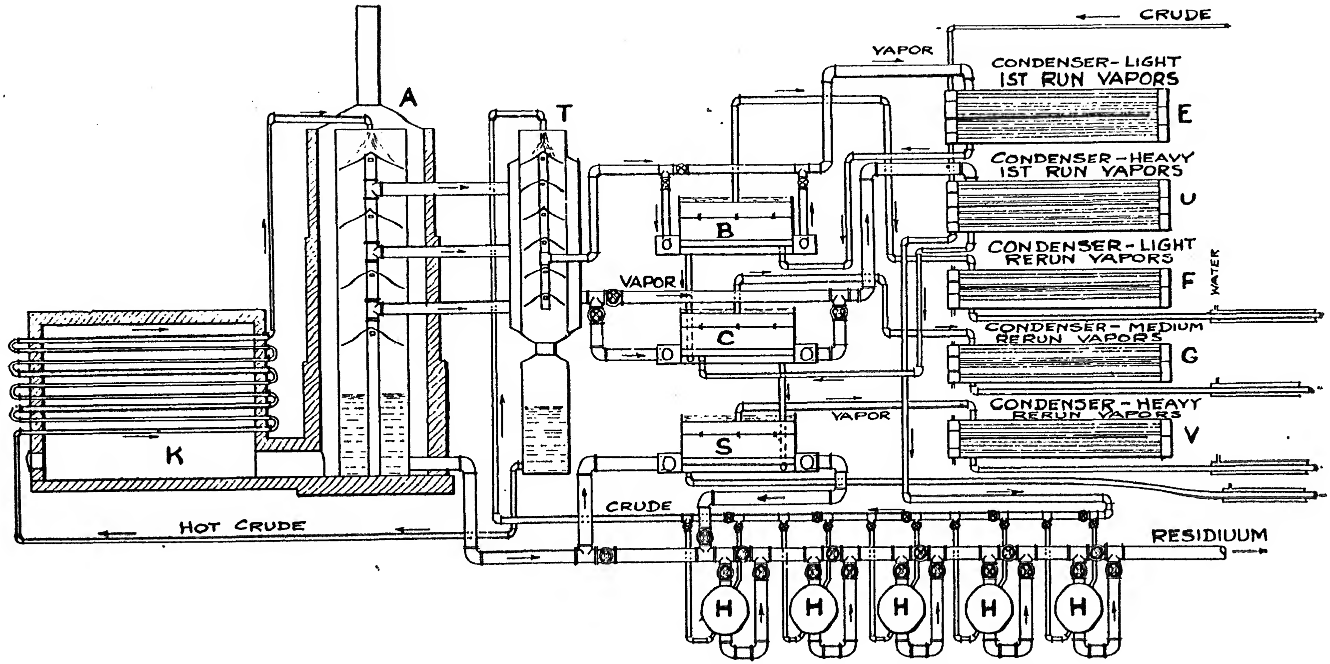


FIG. 39.—Diagram and Flow-Sheet of Trumble Plant at Martinez, Calif.

The oil then flows through the four heat-exchangers, each of which is 4 feet 0 inches in diameter and contains 178 2-inch x 18-foot-0-inch tubes.[12a] The oil enters each exchanger at the bottom, makes six passes, exits from the top and enters the next exchanger. The oil

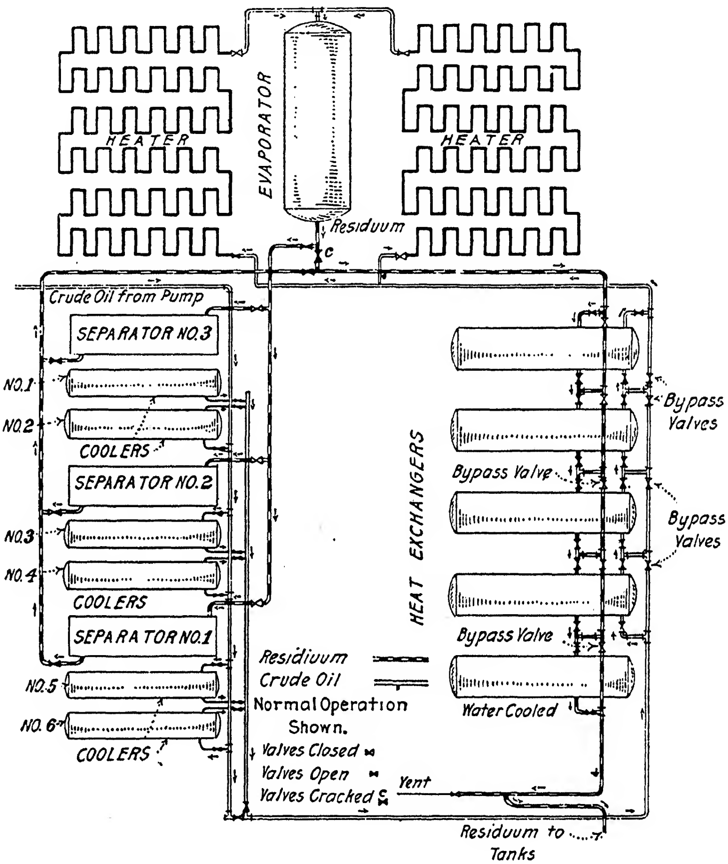


Fig. 40.—Flow of Crude Oil and Residuum in Trumble Plant at Martinez, Calif.

stream is then divided into two equal parts. Each half passes through 72 18-foot-9-inch lengths of 4-inch pipe that are connected, by means of return-bends, into one continuous heating coil. The oil flows back and forth, and upward. When heated to about 450° F. it is discharged into the top of the evaporator. Vapor and residuum are formed here.

[12a] The four-foot exchangers as built by the General Petroleum Corporation contain 258 2-inch tubes as compared to the Shell Company's 178.

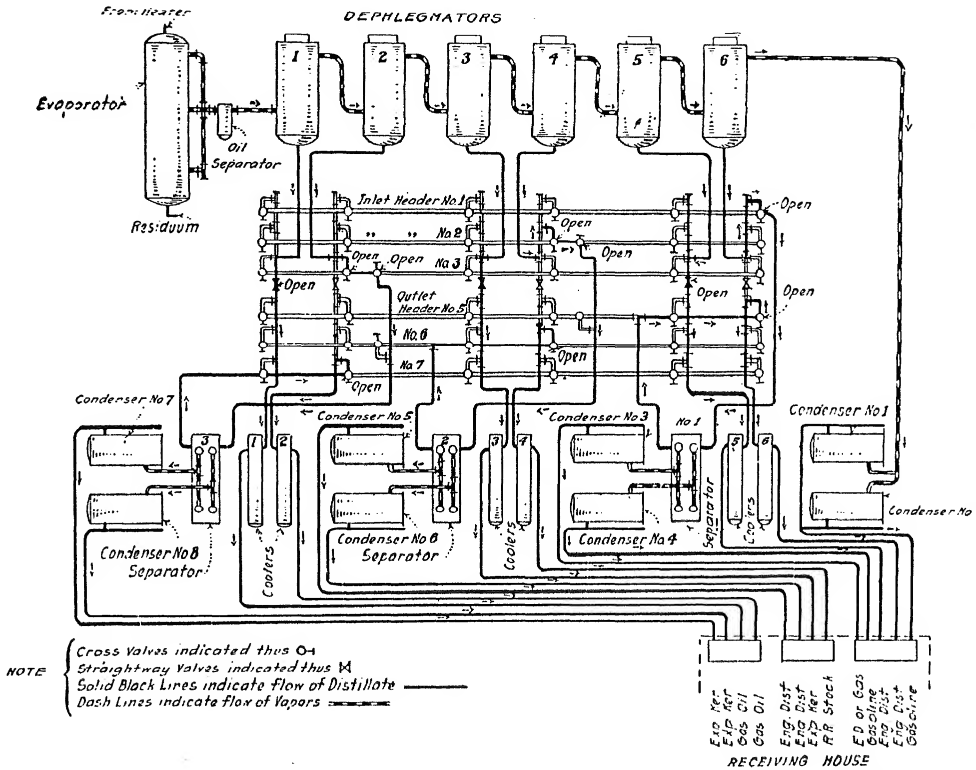


FIG. 41.—Flow of Vapor and Distillates in Trumble Plant at Martinez, Calif.

The residuum is then used as a source of heat for re-running distillates in the separators. Thence it passes to the heat-exchangers, enters at the top, makes two passes around the tubes, and exits from the bottom. In this manner, it passes, in series, through all the exchangers, through a 4-foot tubular water-cooler, through a vented standpipe that controls the level of the residuum in the evaporator, and finally to storage.

The flow of vapor and distillates, and the interconnecting piping, is shown in Figure 41.[13] The evaporator-column is not shown in this flow-sheet, but no special difference in the principles governing the handling of vapors and re-running of distillates is involved in the use of this apparatus.

The vapors from the evaporator are passed through an oil catcher similar to a steam-separator. The entrained oil is returned to the bottom of the evaporator. The vapor passes through six dephlegmators connected in series, entering each at the bottom and leaving at the top. Fractional-condensation occurs in each dephlegmator, forming a liquid that may be a finished product so far as its distillation range is concerned, or that may be a mixture that must be separated into two products. These "dephlegmator-bottoms," as the liquids are called, are run through tubular coolers if they are finished products, or through the separators if they need to be re-run. The vapors from the separators are condensed in tubular condensers.

When the evaporator-column is made part of the plant the vapors from it may be used as a heating means in one or more separators. The uncondensed vapor is then condensed in a water-condenser and re-run in a separator.

The two Trumble plants of the Shell Company, during the first eight months of their operation together, ran an average of 16,000 barrels of crude oil in 24 hours, and vaporized and fractionated 30 per cent of the oil. The fuel consumption was 1.1 per cent of the crude oil run, and the distillation loss was 0.75 per cent. The operation of the two plants required the services of a head stillman, one stillman, and one fireman on each plant, and one receiving-house man on each shift.

General Views of Trumble Plants.

Figures 42 to 45 inclusive show views of the Vernon Trumble Plants. The newer plant at Vernon is a great improvement over these, but the direction of the improvement is much the same as in the Martinez plants. Figures 46 to 51 inclusive show Plants Nos. 1 and 2 of the Shell Company at Martinez, California.

The detailed layout of vapor and distillate piping and apparatus of No. 2 plant at Martinez, in plan and in elevation, is given in *Bulletin 162* of the U. S. Bureau of Mines.

Figure 52 shows a smaller and simplified Trumble plant erected

[13] From Thompson's, N. W., article.

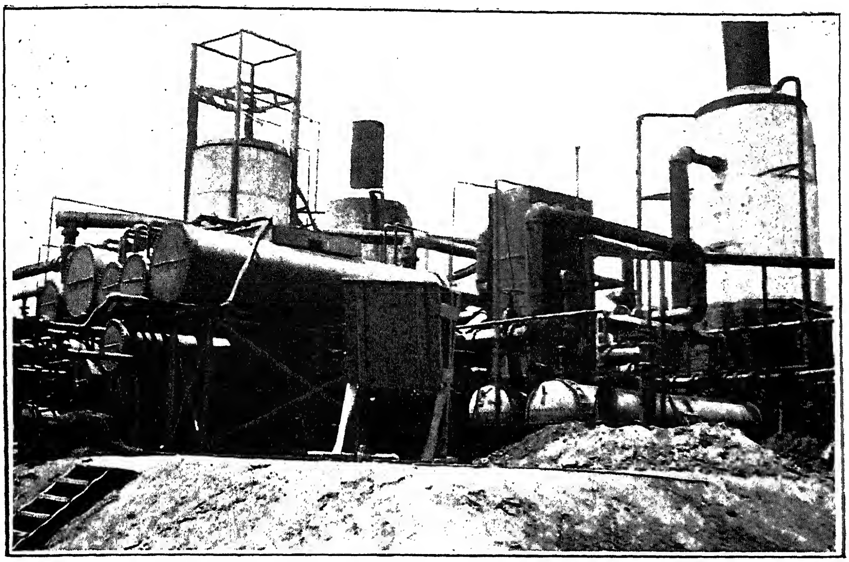


Fig. 42.—Side Elevation of the Condenser Installation, Showing Dephlegmator and Heat Exchangers, Vernon Trumble Plant.

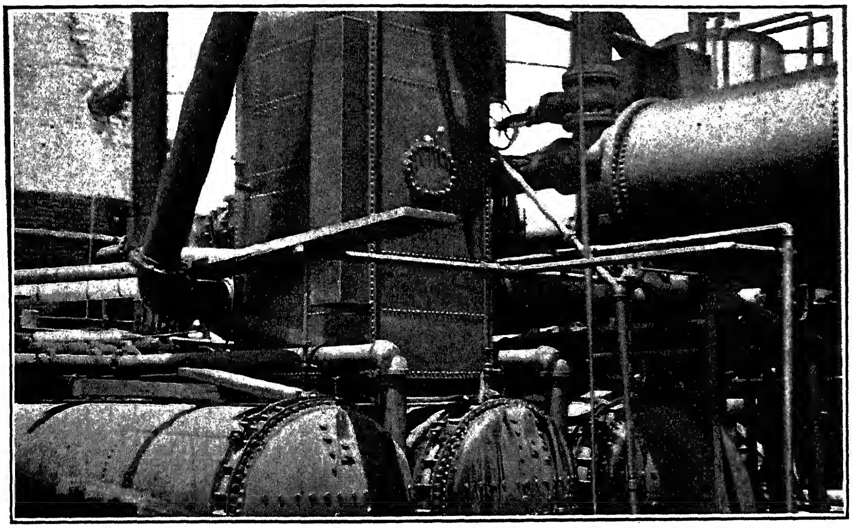


Fig. 43.—Close View of Dephlegmator and Heat Exchangers, Vernon Trumble Plant.

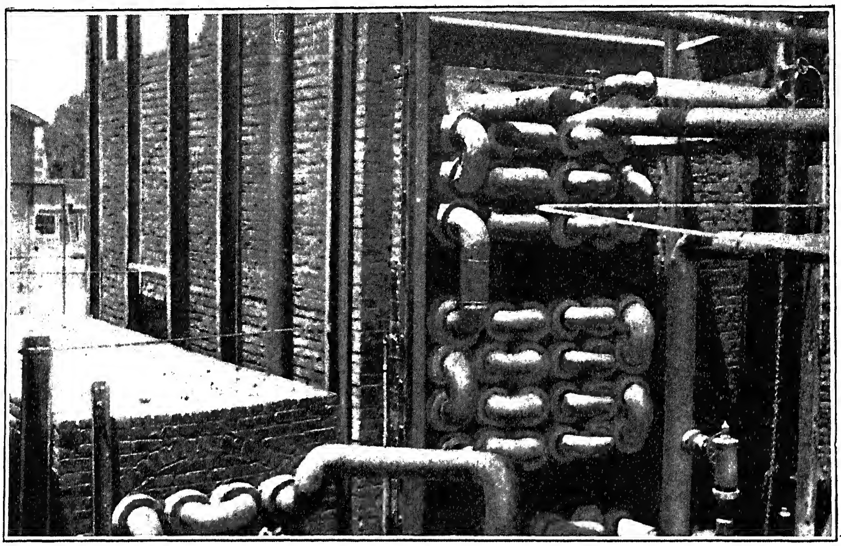
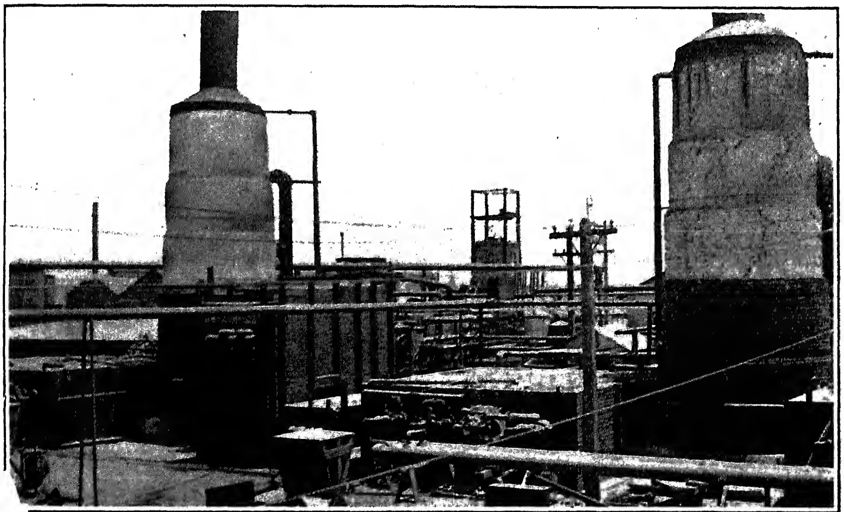


Fig. 44.—Second Type of Heater, Vernon Trumble Plant.



.g. 45.—General View of Pipe Retorts and Evaporators, Vernon Trumble Plant.

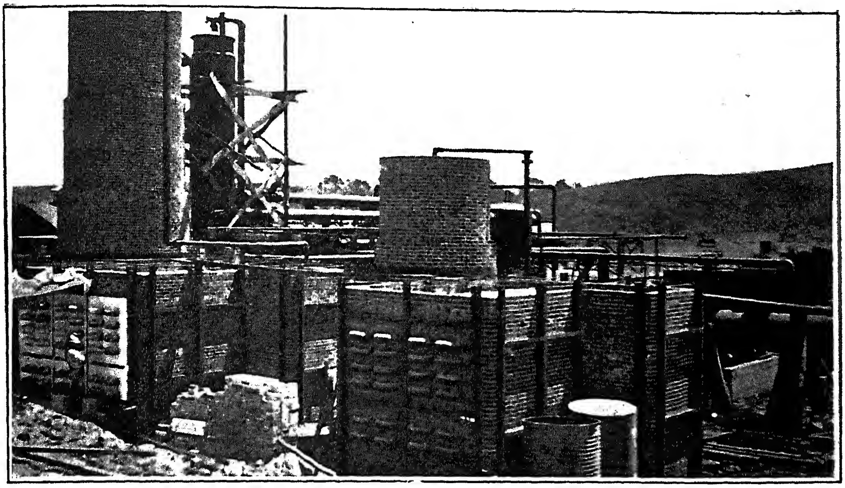


FIG. 46.—Pipe Retorts and Evaporator with Evaporator Column. Trumble Plant No. 1 at Martinez, Calif.

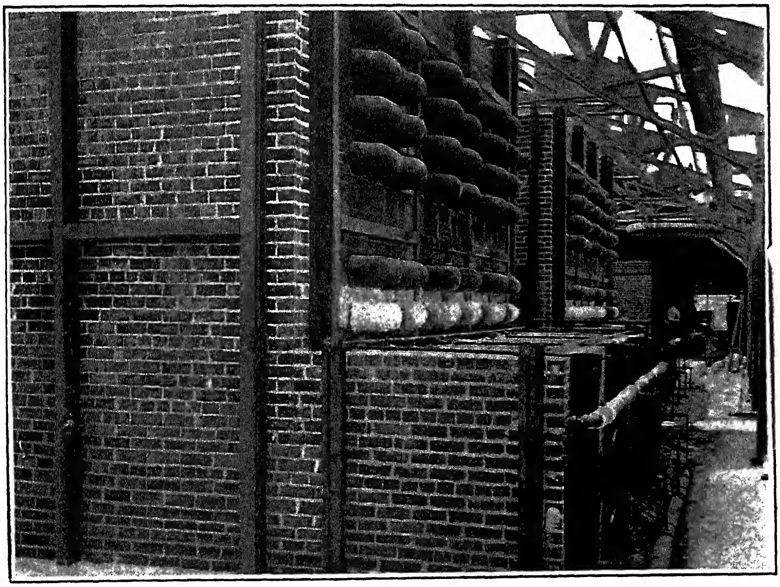


FIG. 47.—Rear View of Pipe Heaters Showing Dutch Ovens. Trumble Plant No. 2 at Martinez, Calif.

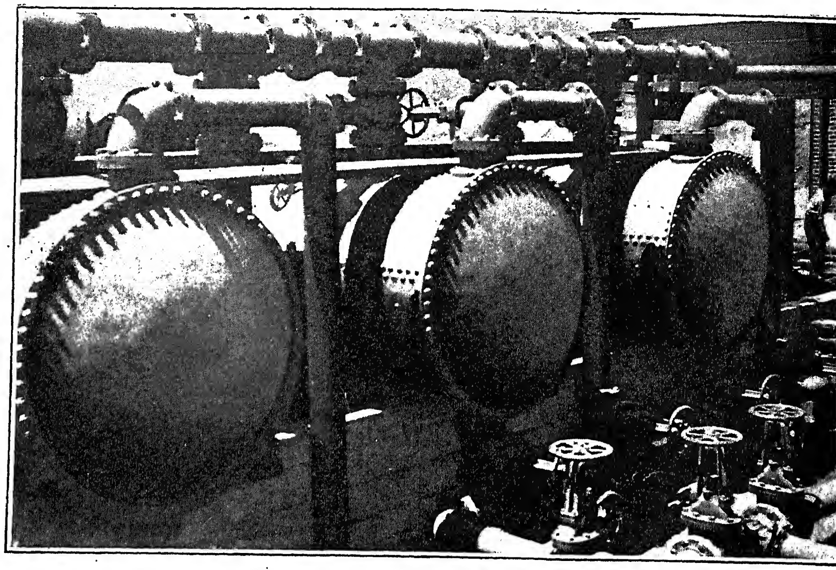


FIG. 48.—Heat Exchangers. Martinez Trumble Plant No. 1.

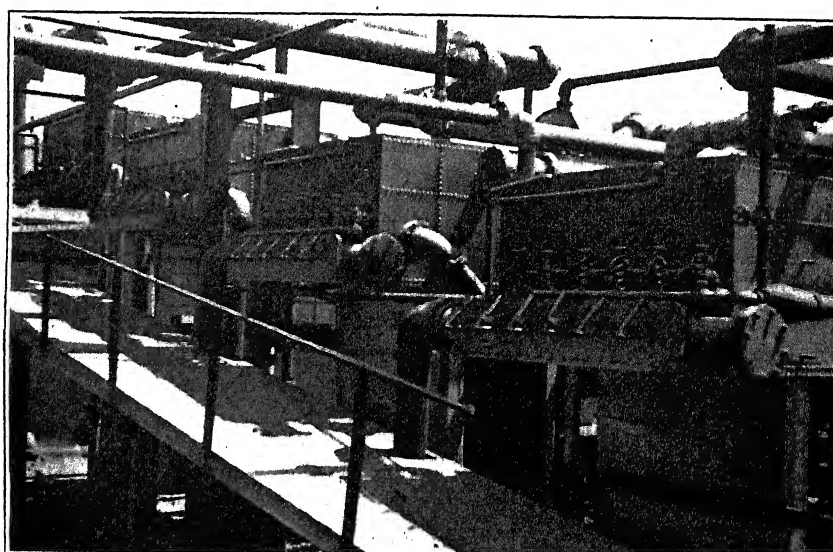


FIG. 49.—Separators Showing Steam Valves and Interconnecting Piping, Martinez Trumble Plant No. 1.

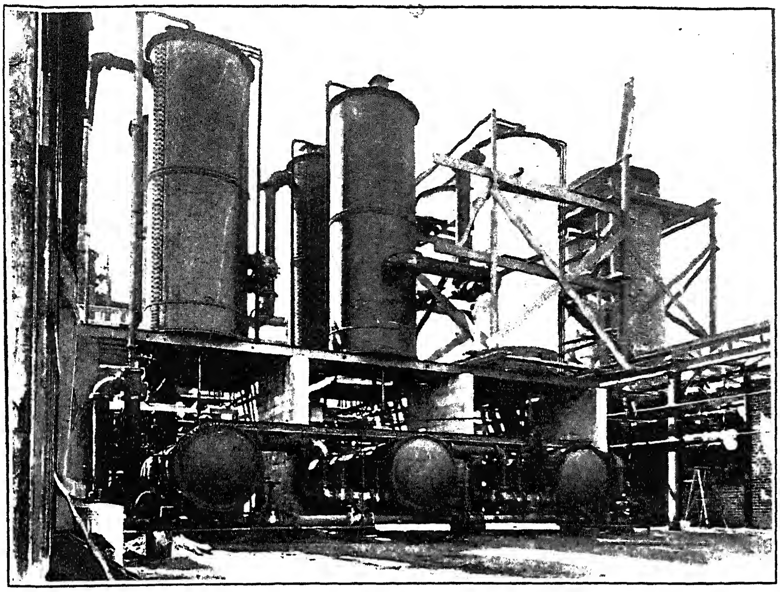


Fig. 50.—General View of Martinez Trumble Plant No. 2 Showing Dephlegmators and Heat Exchangers.

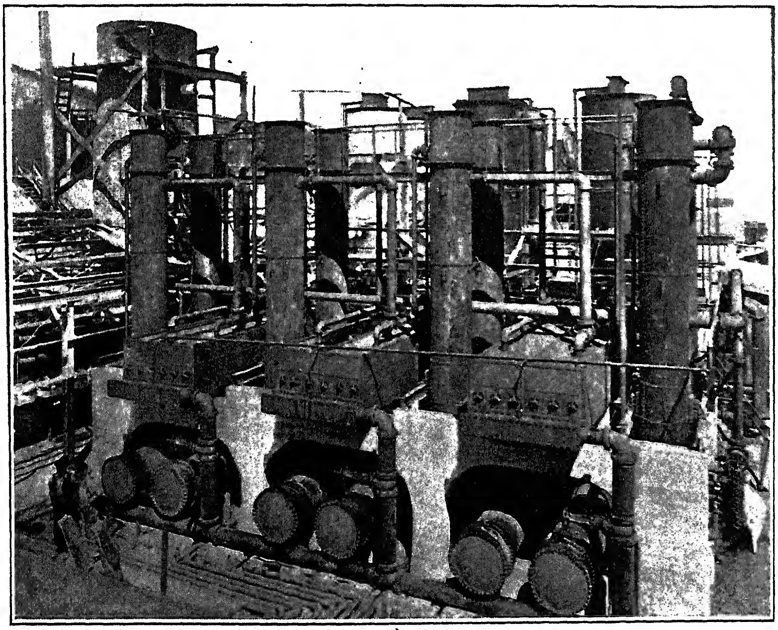


Fig. 51.—General View of Trumble Plant No. 2. Note Run-Down Lines to Tail House in Foreground.

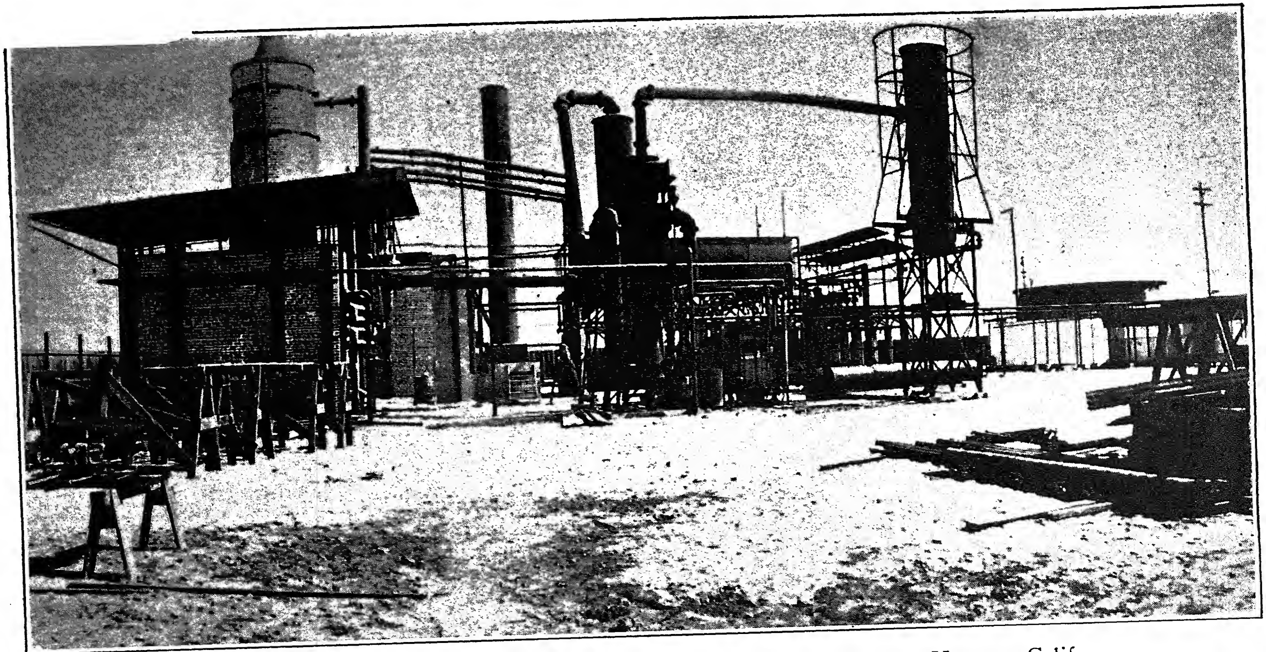


Fig. 52.—Simplified Trumble Plant for Topping Cracked Distillates, Vernon, Calif.

by the General Petroleum Corporation at Vernon, California, to distill "synthetic-crude," i.e., a cracked distillate made from 38° Bé. or "slop distillate" in a vapor-phase cracking plant. The pipe-coil furnace is seen at the left. The evaporator is within the heavy-set brick stack just beyond the furnace. The vapor passes through the two dephlegmators that are seen, one behind the other, in the center of the picture. The lightest vapor is condensed in the tubular water-cooled condenser supported by the light steel framework. Tubular coolers on concrete cradles are seen near the ground beyond the condenser.

The distillation of a light oil is a rather different problem than the distillation of the heavy crudes of California. The volume of vapor is very large and that of residuum small. The plant shown in Figure 52 was intentionally simplified, and is not presented with the idea of illustrating an ideal type, but rather to illustrate the general adaptability of the pipe-still method.

Trumble Plant Details.

The foregoing description of the Vernon and Martinez Trumble plants has dealt mainly with the general layout and flow-sheets. A more detailed, but yet brief, description of the pipe-still furnaces, the evaporator, and the separator will now be given. Details of the heat-exchangers, coolers, condensers and dephlegmators are given in Chapter VII where the evaporator and separator will also be critically discussed.

Pipe-coils and Furnace.

The pipe-coil heaters of the Trumble plants are now made of 4-inch lap-welded pipe, connected by return-bends into one continuous coil. The return-bends are outside the furnace, and are well insulated to prevent heat loss. To facilitate repairs, flanged return-bends should be used on at least one end of the furnace.

The arrangement of the furnace and heating coils in the newer plant of the General Petroleum Corporation at Vernon is shown in Figure 53. The flow of oil through the pipe-coil is back and forth and upward. Gas pockets are thus prevented. Even so, it is probable that the coefficient of heat transfer in the coils would be much higher if an evaporator-column or other apparatus were used to separate the lightest hydrocarbons before the oil passed the pipe-coil heaters. Gas films are excellent heat-insulators.

The furnaces are fired with oil and an ample combustion chamber is provided. The hot gases pass upward and over the pipe coils that contain the hottest oil, then down and around the pipes containing the colder incoming oil, and then to the stack. A large temperature drop between flue gas and oil is thus assured. In this respect the Vernon furnaces are of better design than those of the Martinez plant. The latter are shown in Figure 54.

Wadsworth [14] gives a table showing the temperature of the oil at

[14] *U. S. Bur. Min. Bull. No. 162*, 152.

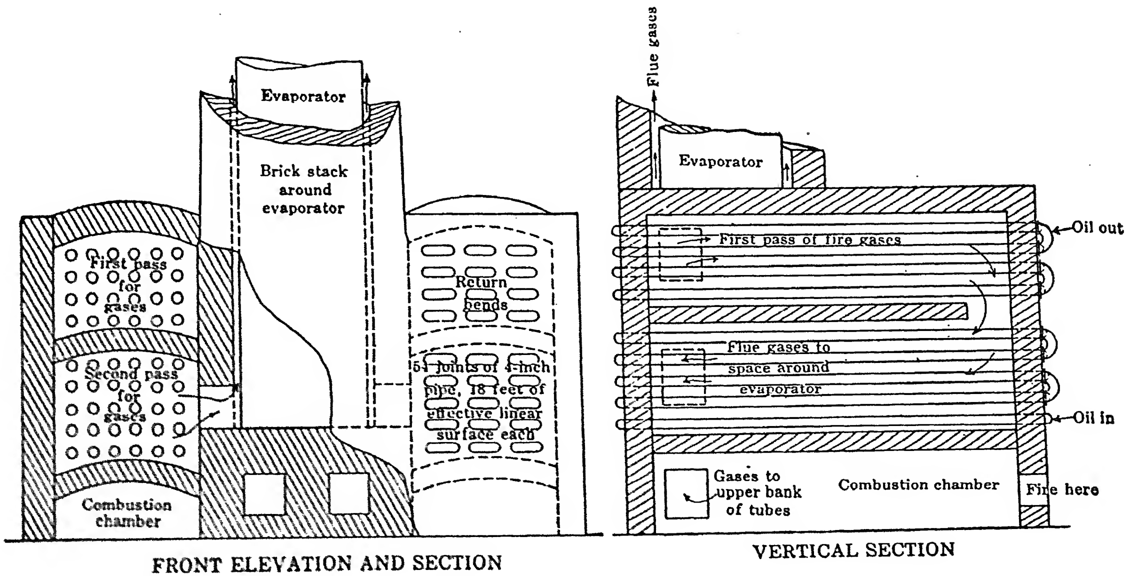


FIG. 53.—Pipe-Retort and Setting, Trumble Plant at Vernon. Has 108 joints of 4-inch pipe with effective length of 1,044 feet. Outside Heating Surface 2,292.4 square feet: Inside Heating Surface 2,050.6 square feet.

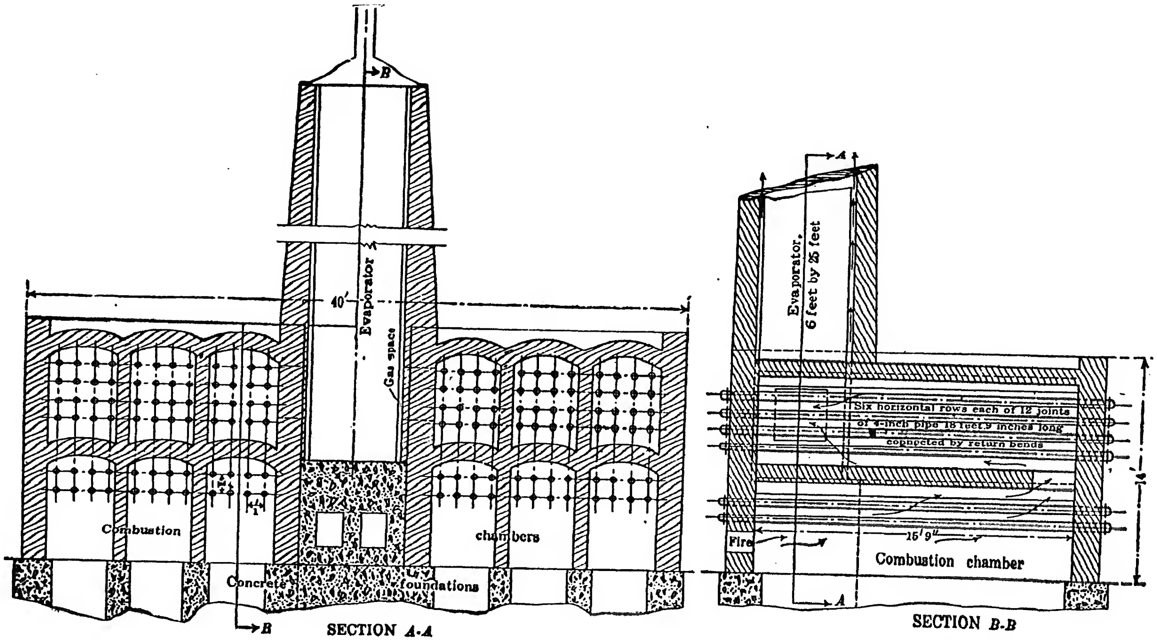


FIG. 54.—Pipe Retorts and Settings of Trumble Plant No. 1 at Martinez. Outside Heating Surface of Pipes 2,728 square feet. Inside Heating Surface 2,430 square feet.

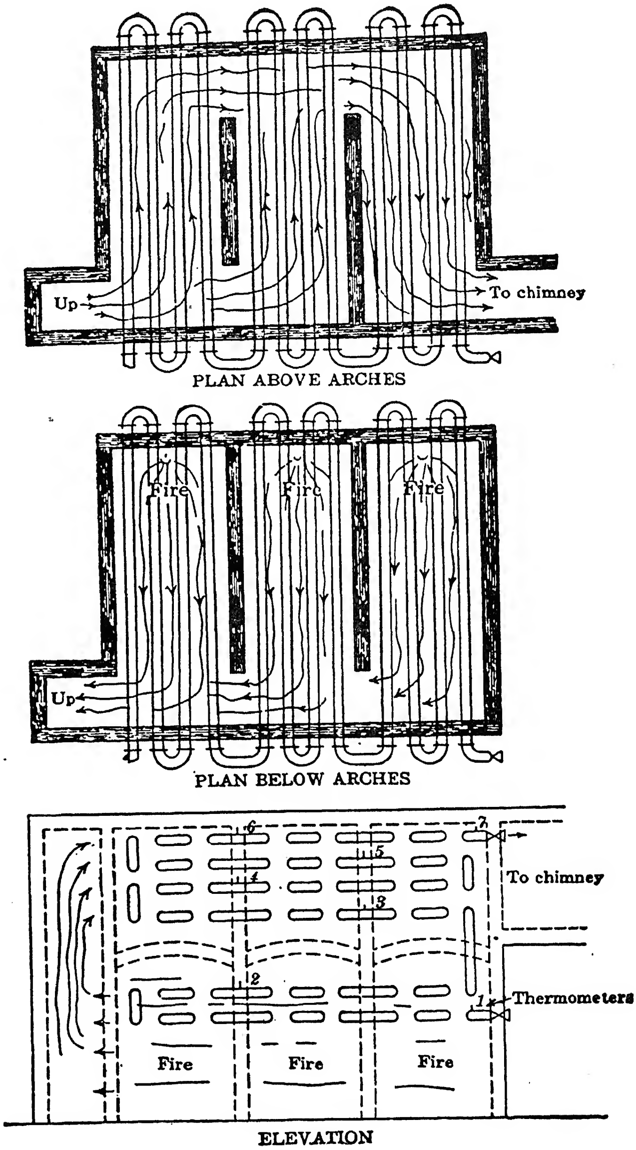


FIG. 55.—Flue-Gas Flow-Sheet, Trumble Plant No. 2 at Martinez, Calif.

TABLE XLI

DATA ON HEATERS AT TRUMBLE PLANT NO. 2, MARTINEZ, CALIF.

AUGUST, 1916

Temperatures given in degrees Fahrenheit

Thermometer No.[a]	9:30 a.m. Temperature	Rise[b]	10 a.m. Temperature	Rise[b]	10:30 a.m. Temperature	Rise[b]	11 a.m. Temperature	Rise[b]	12 noon Temperature	Rise[b]	1 p.m. Temperature	Rise[b]	1:30 p.m. Temperature	Rise[b]	2 p.m. Temperature	Rise[b]	3 p.m. Temperature	Rise[b]	4 p.m. Temperature	Rise[b]
1	198	107	197	109	197	112	217	93	219	95	221	94	220	93	220	92	219	95	219	98
2	305	30	306	30	309	30	310	31	314	31	315	30	313	30	312	31	314	32	317	32
3	335	30	336	30	339	30	341	30	345	30	345	30	343	31	343	31	346	30	349	40
4	365	10	366	10	369	10	371	10	375	10	375	10	374	9	374	9	376	10	389	0
5	375	25	376	26	379	26	381	26	385	26	385	25	383	27	383	26	386	25	389	27
6	400	3	401	2	405	2	407	2	411	2	410	3	410	3	409	4	411	3	416	2
7	403		403		407		409		413		413		413		413		414		418	

[a] See Figure 23 for position of thermometers.

[b] Shows temperature rise from one reading to next reading.

various points in its passage through the pipe-retorts of Martinez Plant No. 2. The temperature of the oil to the retorts as shown in a typical set of readings was 198° F. After flowing through the retorts beneath the arch and through 4 lengths of pipe above the arch, the oil reached a temperature of 335° F. The temperature at which the oil left the furnace was 403° F. Thus the temperature was raised 137° F. in the two lower coils, and only 68° F. in the four upper coils. The increase in temperature in the two upper coils was only 30° F. Had the flow of flue-gas and oil been counter-current, the heat-transfer would have been more complete, and the flue gas would have left the retorts at a lower temperature.

Figure 55 shows the location of the thermometers, Table XLI the tabulated temperature data and Table XLII a summary of design and operating data for Trumble Plant No. 2 at Martinez.

TABLE XLII

DESIGN AND OPERATING DATA, 4-INCH PIPE-RETORTS, TRUMBLE PLANT No. 2, MARTINEZ, CALIF.

Quantity of crude oil heated, 10,000 barrels in 24 hours, of oil of 25.7° Bé (0.900) gravity.

Quantity passed through one heater, 1,093 pounds per minute.

Total length of pipe in one heater, 1,461 feet.

Total length of pipe in one heater exposed to heat, 1,136 feet.

Total area heating surface, 1,486.8 square feet.

Total average rise of temperature, 197° F. (91.65° C.).

Total time required for oil to travel through one heater, 6 minutes and [illegible] seconds.

Velocity of oil, 3.66 feet per second.

Percentage of total area of pipe exposed to heat, 77.75 per cent.

Average square feet of heating surface for each 1° F. rise between thermometers—(For location of thermometers see Figure 23.)

	Square feet
1 and 2	3.6
2 and 3	7.88
3 and 4	8.64
4 and 5	25.91
5 and 6	9.97
6 and 7	57.59

The Trumble Evaporator.

The Trumble evaporator and evaporator-column are shown in Figure 56. The evaporator column is used by the Shell Company, but not by the General Petroleum Corporation. The evaporator consists of a vertical cylindrical steel shell 6 feet 0 inches by 25 feet 0 inches. The top head is removable. The oil enters through a 6-inch pipe and strikes the upper spreader-cone. The spreader-cones are supported by a 12-inch vapor-pipe. The oil flows to the serrated edge of the spreader-cones, and is distributed in such a manner that at least part of it flows down the walls of the evaporator in a thin film. The diameter of the cone is about 2 inches less than the internal diameter of the cylinder. The evaporator is supported in a brick stack whose inside

dimension is approximately 1 foot greater than the outside diameter of the evaporator. The flue gases from the pipe-coil furnaces pass upward through the annular space, and exit from a short steel stack.

The oil enters the top of the evaporator at a temperature of about

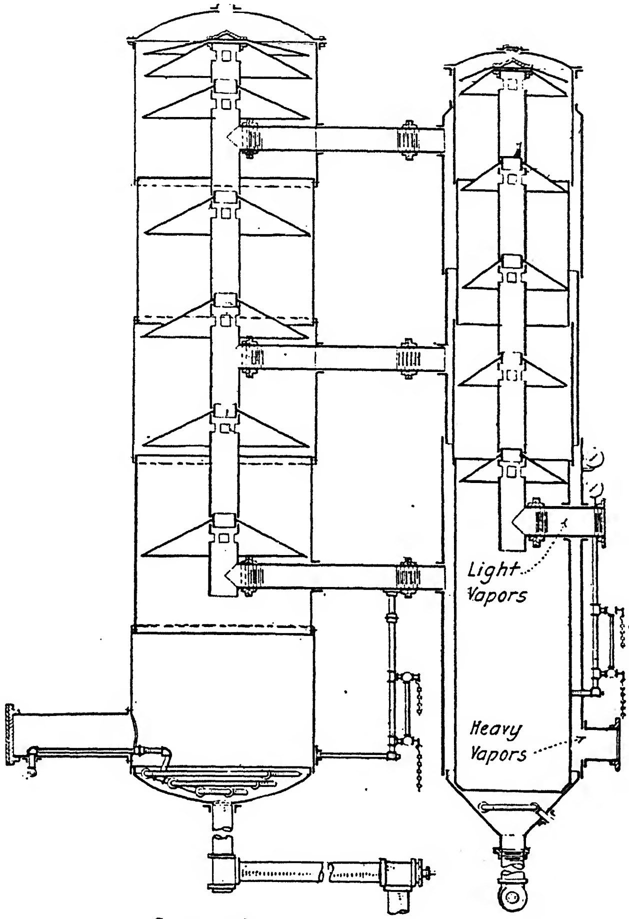
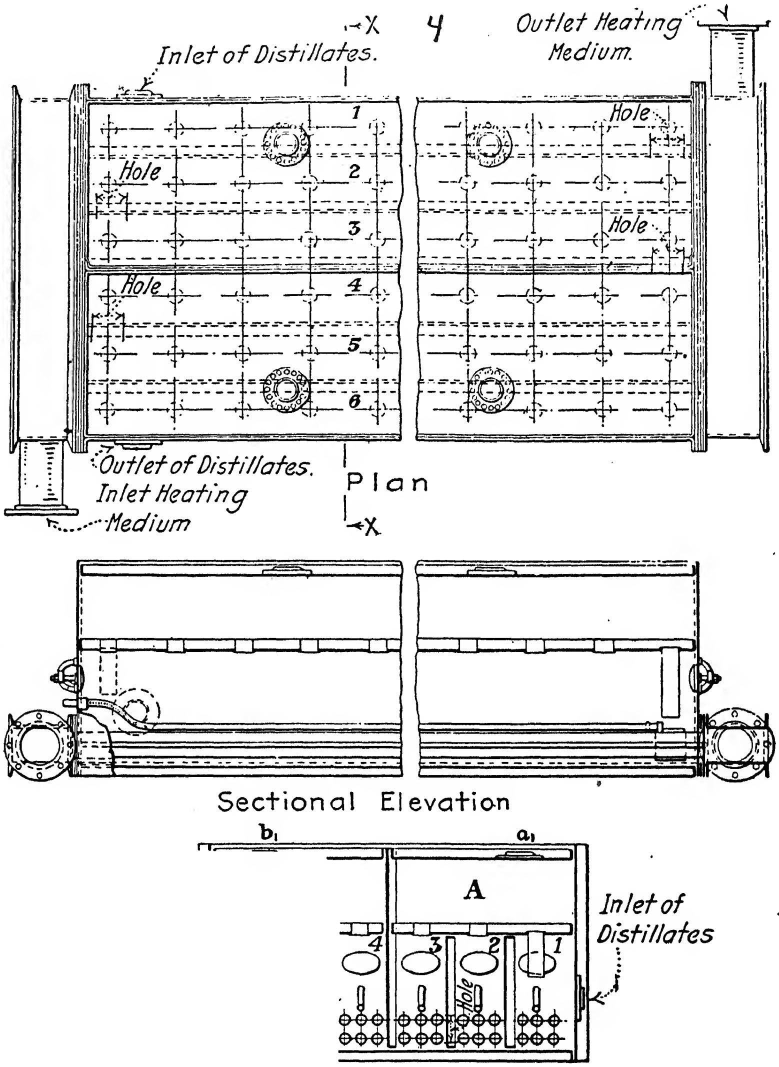


FIG. 56.—Trumble Evaporator and Evaporator Column.

450° F., and with the release of the pressure flashes to form a vapor and a residuum. The vapor enters the central vapor-pipe through the square openings shown in Figure 56. The residuum is heated somewhat as it flows down the side walls of evaporator and collects in the bottom. A constant liquid-level is maintained, and some steam is blown through the hot oil.



Trumble Separator.

ıt the vapor flows through three 10-inch
ınd thence to the dephlegmators or to
ː the vapor from the evaporator enters
:ylindrical steel shells of the evaporator-
:at the oil flowing down the inner wall

of the inside shell. The evaporator-column functions in the same manner as the evaporator, and need not be described in detail.

The spreader-cones and shell of these apparatus should be of substantial construction for they corrode, probably as a result of the action of the vapors from the brine that enters with the oil. The abrasive and corrosive action of the entering oil requires that the upper spreader cone be protected by a heavy steel impingement plate.

The Trumble Separator.

Description of the Trumble separator, or continuous re-run steam-still, might well be postponed and included with the treatment of the general subject of steam-stills. Criticism of the apparatus will be so postponed, but the description will be included here because the apparatus is a distinctive part of the Trumble layout.

A plan view and sectional-elevations of the separator are shown in Figure 57. The separator consists of a rectangular steel box 6 feet 0 inches wide by 18 feet 0 inches long by 3 feet 4 inches deep. The distillate enters compartment (1) and flows in series through the six compartments. The temperature of the liquid is raised during its flow by heat from the 6 boiler-tubes in each section. A single perforated steam-pipe is located just above the heating tubes. The vapor passes from the lower compartment through a series of nipples. The lighter vapors from the first three compartments are combined, as are the heavier vapors from compartments 3 to 6. Before condensation each of these combined vapors is passed through a small dephlegmator to better the fractionation. The dephlegmators used are 2 feet 6 inches by 7 feet 0 inches shells provided with a series of internal steel baffles.

Heat Exchangers, Condensers, Coolers, and Dephlegmators.

The details of these apparatus will not be given here, but such description as may be of value will be included under the general treatment of heat exchangers, condensers, coolers, and fractionating-condensers.

TABLE XLIII

COST DATA AND OPERATING DATA—VERNON TRUMBLE PLANT

The cost[15] of the two original Trumble units at Vernon, California, was as follows:

Two 27,000-barrel residuum tanks	$13,000	
One 15,000-barrel slop-distillate tank	2,200	
Six 1,000-barrel receiving tanks (water-sealed)	6,000	
		$21,200
Evaporators, separators, heat exchangers, condensers, etc., including all apparatus built in the shop	24,000	
Piping and fittings	18,000	
Furnace and brickwork	6,000	
Excavation, erection, labor, foundations	15,800	
		63,800
Total—Distillation plant and tanks		$85,000

These are based on 1912 costs of labor and materials.

[15] *U. S. Bur. Min. Bull. No. 162,* 110.

TABLE XLII—*Continued.*

OPERATING COSTS OF THE VERNON TRUMBLE PLANT, NOVEMBER AND DECEMBER, 1913, AND JANUARY, 1914

(Total oil run, 915,617 barrels)

Power-plant operating expense:		
Material	$251.15	
Labor	1,019.07	
		$1,270.22
Fuel to entire refinery:		
14,153 barrels of 20° Bé. oil, at 56⅔ cents a barrel	$8,018.71	
		$8,018.71
Power-plant maintenance:		
Material	$194.03	
Labor	152.80	
		$346.83
Refinery-apparatus operating expense:		
Material	$64.75	
Labor	1,350.53	
		$1,415.28
Refinery-apparatus maintenance:		
Material	$645.66	
Labor	916.53	
		$1,562.19
Trumble royalty on patent rights		13,267.72
Total expense		$25,880.95
Actual operating expense per barrel of crude run, cents		$\frac{25,880.95}{915,617} = 2.82$
General maintenance:		
Material	$1,281.82	
Labor	2,318.59	
		$3,600.41
Actual maintenance expense per barrel of crude oil run, cents		$\frac{3,600.41}{915,617} = 0.39$
Total operating cost per barrel of crude oil run, cents		3.21
Total fuel used per barrel of crude run:		
Burned under retorts, per cent		0.90
Burned under boilers, per cent		0.64
Boiler equipment		Two 150-horse power Heine boilers.
Boiler pressure		140-pound gage.
Hot-well temperature		180° F.

Plant Efficiency.

The theoretical amount of heat required to remove a 16 per cent cut from one pound of oil has been calculated by Wadsworth.[16]

[16] *U. S. Bur. Min. Bull. No. 162,* 106-7.

PROPERTIES OF CRUDE OIL
(Gravity, 22° Bé. [0.922])

Boiling point		Specific gravity of fraction	Per cent over		Specific gravity of fraction	Per cent of residue	
			By volume	By weight		By volume	By weight
° F.	° C.						
100 to 250	37.8 to 121.1	0.745	0.4	0.326	0.922	98.2	98.16
250 to 300	121.1 to 148.8	.744	4.4	3.70	.928	93.8	94.46
300 to 350	148.8 to 176.6	.802	4.4	3.82	.935	89.4	90.64
350 to 400	176.6 to 204.4	.825	3.6	3.22	.940	85.8	87.42
400 to 450	204.4 to 232.2	.850	3.4	3.14	.945	82.4	84.28
Tops		.....	16.2	.....	.....	....	.....
Water		.....	1.4	1.51	.920	98.6	98.49

Assume:

	B.t.u.
Specific heat of the crude (average value)	0.45
Latent heat of distillate (average value)	125.00
Specific heat of the vapors (average value)	.50
Specific heat of saturated steam	.48

Then:

Heat theoretically required to remove 16 per cent cut

		B.t.u.
To heat 0.982 pound of oil 250° to 300° F. (121.1° to 148.8° C.)	0.982 (250-300) × 0.45 =	22.10
To evaporate 0.037 pound of vapors	.037 × 125 =	4.62
To superheat 0.043 pound of vapors 250° to 300° F. (121.1° to 148.8° C.)	.043 (250-300) × 0.5 =	1.15
To heat 0.945 pound of oil 300° to 350° F. (148.8° to 176.6° C.)	.945 (250-300) × 0.45 =	21.30
To evaporate 0.0382 pound of vapors	.0382 × 125 =	4.78
To superheat 0.081 pound of vapors 300° to 350° F. (148.8° to 176.6° C.)	.081 (300-350) × 0.5 =	2.01
To heat 0.906 pound of oil 350° to 400° F. (176.6° to 204.4° C.)	.906 (350-400) × 0.45 =	20.40
To evaporate 0.032 pound of vapors	.032 × 125 =	4.00
To superheat 0.113 pound of vapors 350° to 400° F. (176.6° to 204.4° C.)	.113 (350-400) × 0.5 =	2.83
To heat 0.874 pound of oil 400° to 450° F. (204.4° to 232.2° C.)	.874 (400-450) × 0.45 =	19.65
To evaporate 0.031 pound of vapors	.031 × 125 =	3.88
To superheat 0.144 pound of vapors 400° to 450° F. (204.4° to 232.2° C.)	.144 (400-450) × 0.5 =	3.60
To superheat 0.0151 pound of steam 250° to 450° F. (121.1° to 232.2° C.)	.015 (250-450) × 0.48 =	1.48
Total heat required to top 1 pound of 18.8° Bé. (specific gravity, 0.941) oil at 100 per cent efficiency		111.80
Total heat required to top 1 barrel of 18.8° Bé. (specific gravity 0.941) oil at 100 per cent efficiency would be 330 pound × 111.80 B.t.u.		36,894.00

Over-all Efficiency of the Topping Plant.

The average fuel consumption on the retort is 0.9 per cent of the crude run, or 0.009 barrel of fuel oil to 1 barrel of oil topped, which, with 15° Bé. fuel oil, is 56675.7 B.t.u., or 14283.1 calories.

The over-all efficiency of the battery of retorts is, therefore,

$$\frac{36894.0 \text{ B.t.u.}}{56675.7 \text{ B.t.u.}} = \frac{9301.0 \text{ cal.}}{14283.1 \text{ cal.}} = 65.3 \text{ per cent}$$

In much the same manner, the efficiency of a Trumble plant at Coalinga was calculated to be 66 per cent. This plant was of improved design, built between May and December, 1915, the cost (exclusive of tankage) $7.48 per barrel of normal daily capacity.

Cost and Operation of Trumble Plants at Martinez.

The plants at Martinez have been operated almost continuously since they were built. The lower heater pipes have burned out and there have been other minor troubles, but these have caused but brief shutdowns. Table XLIV [17] presents a record of one month's operation.

TABLE XLIV

Record of One Month's Operation, Trumble Plants Nos. 1 and 2, Martinez, Calif.

Crude oil Topped by Both Plants	Gravity		Name of Product	Volume Produced	Gravity		Percentage of Product of Total Crude
	° Bé.	Specific Gravity			° Bé.	Specific Gravity	
Barrels				*Barrels*			
51,327.96	23 to 28	0.916 to 0.987	Gasoline	10,660.53	58	0.747	2.46
279,896.18	22 to 23	.922 to .916	Engine distillate	10,064.47	50	.779	2.35
103,658.52	20	.934	Domestic kerosene	475.19	44	.806	.11
434,882.66			Export kerosene	33,122.99	39.5	.827	7.63
			Stove distillate	25,891.31	33	.859	5.82
			Residuum	350,658.86	17 to 21	0.953 to 0.928	80.6

Fuel consumed, per cent of crude run	1.1
Refining loss, barrels	4,109.31
Refining loss, per cent	.94
Steam consumed, pounds of water	2,811,510
Boiler horse power developed per day	113
Cooling water used, barrels	2,174,400

[17] *U. S. Bur. Min. Bull. No. 162,* 148.

Table XLV [18] is a tabulation of the cost of construction of the No. 2 plant at Martinez, based on material and labor costs of 1915. Excluding tankage the cost was approximately $8.80 per barrel of daily capacity.

TABLE XLV

Cost of Construction of Trumble Plant No. 2, Martinez, Calif.

Three inspection boxes	$1,125.83
Six 30-inch coolers, three 6 by 18 foot separators, eight 30-inch vertical condensers	10,006.95
Five 48-inch heat-exchangers, and six dephlegmators	4,098.00
One 6-foot by 25-foot evaporator	842.50
One 12-inch oil separator	265.00
One 470-barrel fuel oil tank	558.50
Two 2,800-barrel residuum tanks	3,945.90
Five 1,000-barrel distillate receiving tanks	5,472.50
Miscellaneous equipment	55.45
Building and platforms	5,720.34
Heaters and brickwork	4,010.34
Pipe and fittings	13,850.84
Excavation, foundations and erecting labor	17,591.57
Total	$69,178.18
10 per cent for engineering and supervision	6,917.81
	$76,095.99

The efficiency of the plant has been calculated by Wadsworth.[19] The nature of the crude oil is shown by the distillation data of Table XLVI.

TABLE XLVI

Composite Sample of Crude Oil—28° Bé., Sp. gr. 0.922

Temperature ° F.	Sp. Gr. of the Fraction	Per Cent Vaporized		Sp. Gr. of Residue	Per Cent of Residue	
		By Volume	By Weight		By Volume	By Weight
100-225	0.730	1.86	1.25	0.927	98.14	98.75
225-250	.750	1.50	1.03	.929	96.64	97.72
250-300	.770	3.71	2.64	.935	92.93	95.08
300-350	.820	5.19	3.92	.942	87.74	91.16
350-400	.850	5.50	4.32	.948	82.24	86.84
400-450	.855	1.00	0.79	.950	81.24	86.05

The quantity of heat required to remove the fractions shown in Table XLVI from one pound of this oil is shown in Table XLVII. The heat recovered in the exchanger is considered, and it is assumed that:

The specific heat of the oil is 0.45, approximately.

The specific heat of the vapors is 0.50, approximately.

The latent heat of the distillate is 125 B.t.u., approximately.

The oil leaves the last exchanger at 225° F. (107.2° C.).

[18] *U. S. Bur. Min. Bull. No. 162,* 149.

[19] *U. S. Bur. Min. Bull. No. 162,* 150-51.

TABLE XLVII

CALCULATION OF THEORETICAL FUEL CONSUMPTION AND OVER-ALL EFFICIENCY OF TRUMBLE PLANTS NOS. 1 AND 2, MARTINEZ, CALIF.

		B.t.u.
Heat 0.988 pound of oil 225 to 250° F. (107.2 to 121.1° C.)	0.988 (225-250) × 0.45	= 11.21
Evaporate 0.013 pound of vapors	.013 × 125	= 1.63
Superheat 0.023 pound of vapors 225 to 250° F. (107.2 to 121.1° C.)	.023 (225-250) × 0.50	= 0.03
Heat 0.977 pound of oil 250 to 300° F. (121.1 to 148.8° C.)	.977 (250-300) × 0.45	= 22.00
Evaporate 0.026 pound of vapors	.026 × 125	= 3.25
Superheat 0.049 pound of vapors 250 to 300° F. (121.1 to 148.8° C.)	.049 (250-300) × .50	= 1.25
Heat 0.951 barrel of oil 300 to 350° F. (148.8 to 176.6° C.)	.951 (300-350) × .45	= 21.40
Evaporate 0.039 pound of vapors	.039 × 125	= 4.87
Superheat 0.088 pound of vapors 300 to 350° F. (148.8 to 176.6° C.)	.088 (300-350) × .50	= 2.20
Heat 0.912 pound of oil 350 to 400° F. (176.6 to 204.4° C.)	0.912 (350-400) × 0.045	= 20.50
Evaporate 0.043 pound of vapor	0.043 × 125	= 5.37
Superheat 0.131 pound vapor 350 to 400° F.	0.131 (350-400) × 0.50	= 3.27
Heat 0.868 pound of oil 400 to 450° F. (204.4 to 232.2° C.)	0.868 (400-450) × 0.45	= 19.32
Evaporate 0.008 pound of vapor	0.008 × 125	= 1.00
Superheat 0.139 pound of vapor 400 to 450° F.	0.139 (400-450) × 0.50	= 3.48
Total heat required to top 1 pound of this oil at 100 per cent efficiency		120.78
And since 22° Bé. (0.922 sp. gr.) gravity oil weighs 322.5 pounds per barrel, to top 1 barrel would require 322.5 × 120.78 B.t.u.		= 38,951.6 B.t.u.
Actual consumption of fuel oil (18° Bé.) per barrel of oil topped was 0.011 bbl. This is equivalent to		68,325.4 B.t.u.

Over-all efficiency of the Retorts is $\frac{38{,}951.6}{68{,}325.4} = 57$ per cent

Thus, the efficiency of the Martinez plants is seen to be somewhat s than that of the Vernon and Coalinga plants. The furnace design " be responsible for this as has already been suggested.

ederer Topping Plant of the Atlantic Gulf Oil Corporaion.[20]

pipe-still topping plants of the Atlantic Gulf Oil Corporation several novel features. One of these plants is located at ti, State of Vera Cruz, Mexico, and the other at Fawley, near

e accompanying description of the topping plants of the Atlantic Gulf oration is based on data furnished by Dr. E. R. Lederer, formerly of the Refining Department of this corporation. The plant was by Dr. Lederer and his engineering staff in collaboration with the engithe Power Specialty Company. It is a pleasure to acknowledge Dr. generosity in furnishing this material.

Southampton in England. The oil handled is a 21° Bé. light Mexican crude. The normal capacity of the Mexican plant with four pipe-still furnaces is 12,000 barrels of oil per day of 24 hours. A general view of the Mexican plant is shown in Figure 58. The four pipe-stills are seen in the foreground.

Each furnace contains 1150 lineal feet of 4-inch pipe-section with a total external heating surface of 14,000 square feet. The pipe-section [21] is of the type used in the Foster superheater. A cold-drawn seamless steel tube is expanded into corrugated cast-iron sleeves so that a metal-to-metal contact is obtained. The heating surface per lineal foot is approximately four times that of the plain tube. Furthermore cast-iron is far more resistant to the oxidizing effect of the hot flue-gases. Scaling is largely avoided, and the life of the heating element greatly prolonged. The ends of the seamless tube are expanded into cast-steel return headers. In this manner the elements are connected into one continuous coil. Figure 59 shows the construction of the coil, Figure 60 two handhole cap details and Figure 61 a pipe-still heating element assembled for shipment. The tubes are fitted with rectangular plates at each end so that they can be built up one above the other and supported from the bottom. Opposite the end of each tube is a handhole that allows easy access to the tube.

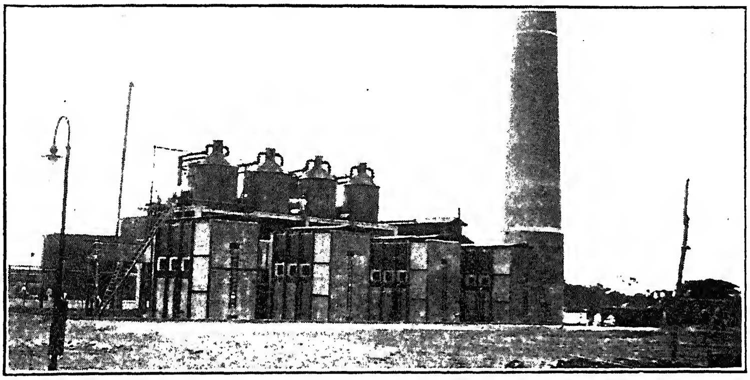


FIG. 58.—Lederer Plant of Atlantic Gulf Oil Co. at Tecomate, Mexico.

The entire heating element is so placed in the furnace that all the joints and handholes are outside the lining of the furnace chambers, and are protected by the rectangular cast-iron plates near the end of each tube. A sectional elevation and plan of a pipe-still furnace as built by the Power Specialty Company is shown in Figure 62.

The oil enters the heating element at 400° F. The velocity of the oil in the pipe-still is maintained above the critical velocity. The pressure required to force the oil through the coil is 50 pounds. The

[21] Manufactured by the Power Specialty Company of New York.

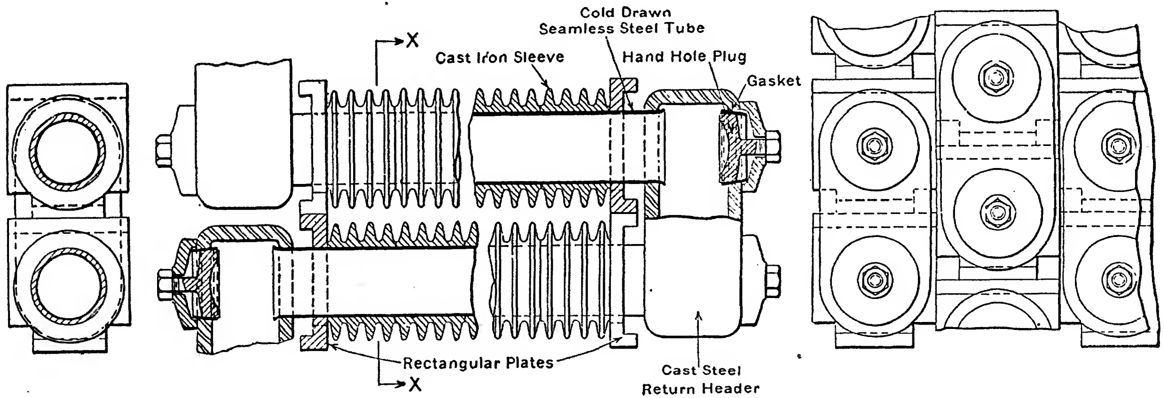


FIG. 59.—Construction of Foster Heating Surface Showing Details of Tubes, Headers and Plates.

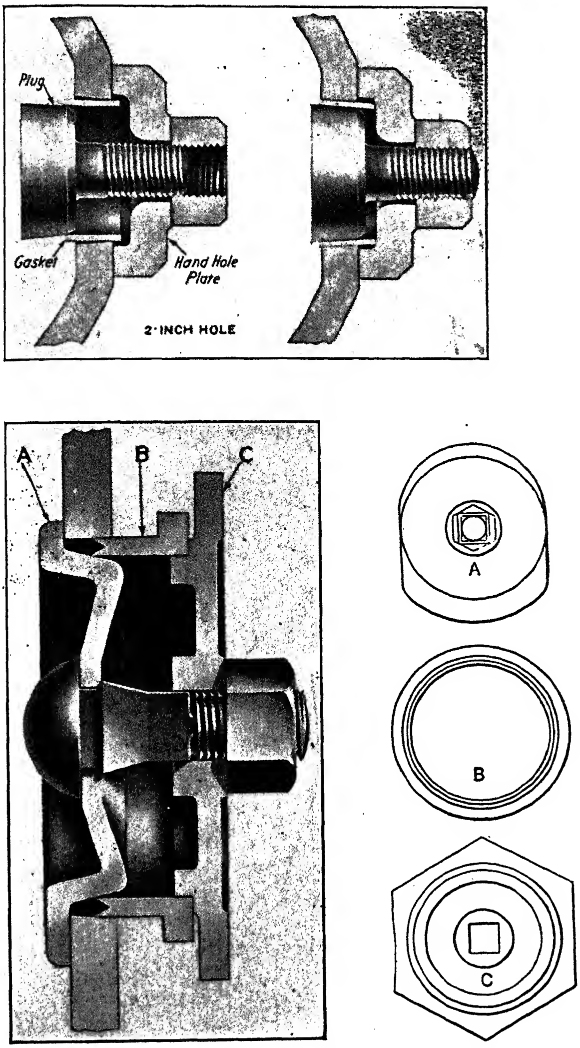


FIG. 60.—Handhole Cap Details, Foster Heater.

theoretical heat required to remove a 15 per cent cut is 146.1 B.t.u. per pound of oil. The temperature of the flue-gas leaving the combustion-chamber is 1700° F., and of the flue-gas leaving the furnace 650° F.

The theoretical heat requirement to remove a 15 per cent cut by weight is calculated as follows:

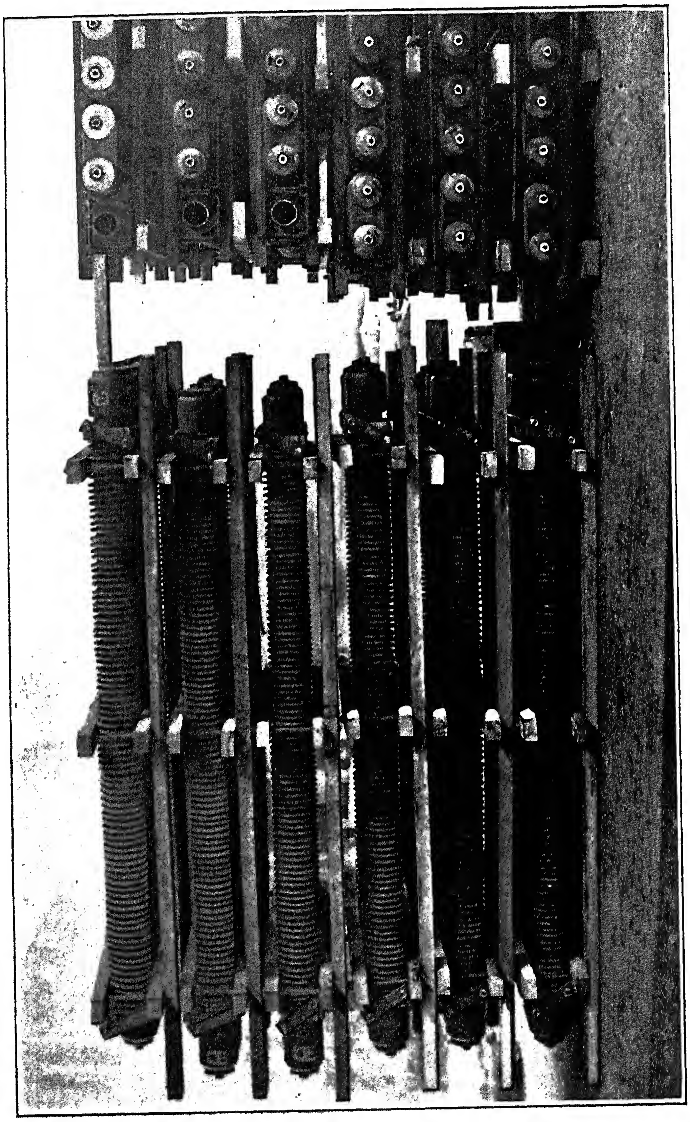
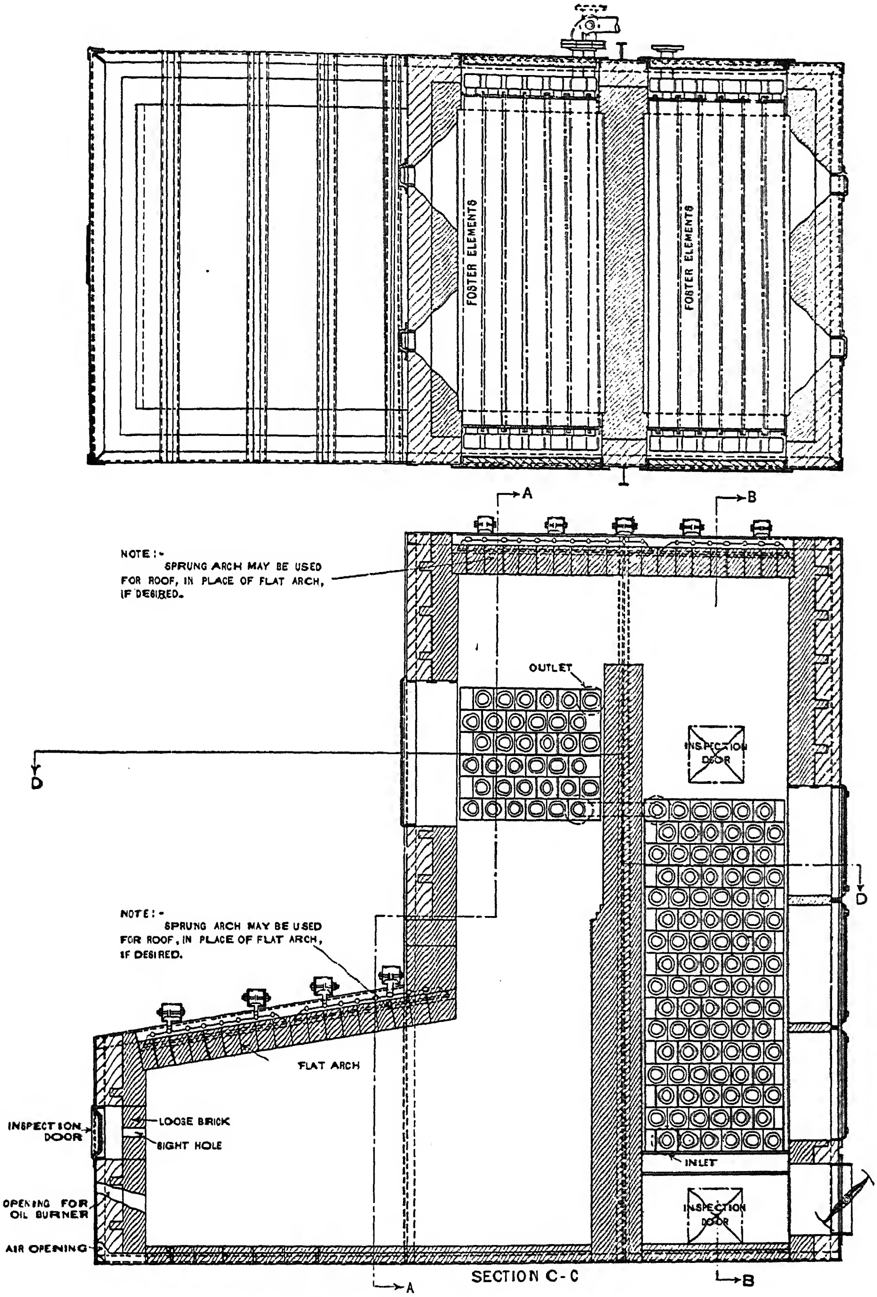


FIG. 61.—Foster Pipe-Still Heating Elements Assembled for Shipment.



Still designed for topping crude oil.

FIG. 62.—Sectional Elevation and Plan of Pipe-Still Furnace as Built by the Power Specialty Company.

Temp. ° F.	Per cent by weight of oil evaporated	Per cent by weight of residuum
100-225	1.25	98.75
225-250	1.03	97.72
250-300	2.64	95.08
300-350	5.08	90.00
350-400	5.00	85.00

Assume:

Specific heat of crude oil and distillates...... 0.45 B.t.u. per lb.
Specific heat of vapors........................ 0.50 B.t.u. per lb.
Latent heat of Vaporization................. 125.0 B.t.u. per lb.

Then heat requirement is:

To raise temperature of the oil:

$$
\begin{array}{llll}
118^\circ \text{ F.}-225^\circ \text{ F.} & = 1.000 \times 107 \times 0.45 = & 48.10 & \text{B.t.u.} \\
225 \quad -250 & = 0.988 \times 25 \times 0.45 = & 11.13 & \text{B.t.u.} \\
250 \quad -300 & = 0.977 \times 50 \times 0.45 = & 22.01 & \text{B.t.u.} \\
300 \quad -350 & = 0.951 \times 50 \times 0.45 = & 21.40 & \text{B.t.u.} \\
350 \quad -400 & = 0.900 \times 50 \times 0.45 = & 20.26 & \text{B.t.u.}
\end{array}
$$

To form the vapor:

$$= 0.15 \times 125.0 \text{ B.t.u.} = 18.75 \text{ B.t.u.}$$

To raise temperature of the vapor:

$$
\begin{array}{llll}
225^\circ \text{ F.}-250^\circ \text{ F.} & = 0.012 \times 25 \times 0.50 = & 0.15 & \text{B.t.u.} \\
250 \quad -300 & = 0.023 \times 50 \times 0.50 = & 0.58 & \text{B.t.u.} \\
300 \quad -350 & = 0.049 \times 50 \times 0.50 = & 1.23 & \text{B.t.u.} \\
350 \quad -400 & = 0.100 \times 50 \times 0.50 = & 2.50 & \text{B.t.u.}
\end{array}
$$

Total B.t.u. required......... 146.11

The approximate fuel consumption may be calculated as follows:

Assume:

Oil to be distilled = 40,700 lbs. per hour
Temperature of air 90° F.
Temperature of flue gas 650° F.
Excess of air over theoretical requirement = 50 per cent
Chemical composition of fuel oil:—

	Per cent
Carbon	87
Hydrogen	12
Other	1

Net Heating Value of fuel oil 18,000 B.t.u. per lb.
Specific heats at constant pressure over the range 0° F. to 650° F.:

	Calories per Gram	B.t.u. per Pound
N_2, O_2	0.249	0.448
CO_2	0.217	0.391
H_2O	0.472	0.849

Radiation loss = 10 per cent of total heat supplied.

Then in the combustion of one pound of fuel oil there is produced

$$0.87 \times \frac{CO_2}{C} = 0.87 \times \frac{44}{12} = 3.19 \text{ lbs. of } CO_2$$

$$0.12 \times \frac{H_2O}{2H} = 0.12 \times \frac{18}{2} = 1.08 \text{ lbs. of } H_2O$$

The theoretical weight of oxygen required to burn one pound of fuel is:

$$(0.87 \text{ lb.} \times \frac{32}{12}) + (0.12 \text{ lb.} \times 8) = 3.28 \text{ lbs.}$$

Since air is 23 per cent O_2 by weight, the theoretical weight of air required to burn one pound of fuel is $3.28 \text{ lbs.} \times \frac{100}{23} = 14.26$ lbs. The flue gas resulting from the combustion of one pound of fuel is thus composed of:

	Pounds
CO_2	3.19
H_2O	1.08
N_2	10.98
Air ($O_2 + N_2$)	7.13

or better:

	Pounds
CO_2	3.19
H_2O	1.08
N_2	16.47
O_2	1.64

The heat content of the flue gas formed per pound of fuel oil burned is:

$$\begin{aligned}
3.19 \times 560 \times 0.391 \text{ B.t.u.} &= 698 \text{ B.t.u.} \\
1.08 \times 560 \times 0.849 \text{ B.t.u.} &= 513 \text{ B.t.u.} \\
16.47 \times 560 \times 0.448 \text{ B.t.u.} &= 4{,}132 \text{ B.t.u.} \\
1.64 \times 560 \times 0.448 \text{ B.t.u.} &= 412 \text{ B.t.u.} \\
\hline
& 5{,}755 \text{ B.t.u.}
\end{aligned}$$

Let "x" equal the weight in pounds of fuel-oil required per hour. The total B.t.u.'s furnished is thus 18,000x. The B.t.u.'s in the flue-gas are 5,755x. The B.t.u.'s absorbed by the oil in one hour is equal to $40{,}700 \times 146.11$ B.t.u. $= 5{,}946{,}667$ B.t.u. The loss by radiation is $0.1 \times 18{,}000x$.

Equating:

$$\begin{aligned}
18{,}000x &= 5{,}755x + 5{,}946{,}667 + 1{,}800x \\
10{,}445x &= 5{,}946{,}667 \\
x &= 569.3 \text{ pounds of fuel oil per hour, or} \\
&= 1.63 \text{ barrels of fuel oil per hour.}
\end{aligned}$$

This is approximately 1.3 per cent by volume of the crude oil run through the pipe-still. If the furnace efficiency is expressed as the ratio of the heat actually absorbed by the oil to the total heat supplied

it should be recalled that the flue-gases are discharged at 650° F., and that no allowance has been made for recovery of heat from the residuum (oil enters furnace at 118° F. rather than at 250° F. as in the Trumble plants). The flue-gas may just as well be discharged at 350 to 400° F. if waste-heat boilers were used or if the oil-heating surface were increased. If the oil entered the heating-units at 250° F. in place of 118° F. the over-all heat efficiency of the plant would be increased. The amount of the increase cannot be calculated because the heat transfer in the pipe-still would be less when the temperature difference between flue-gas and oil was less.

The coefficient of heat transfer H may be calculated as follows:

Let

H = B.t.u. per sq. ft. per hr. per 1° F. temperature difference.
W = weight of oil heated in pounds per hour.
t_i' = initial temperature of the oil.
t_f' = final temperature of the oil.
t_i'' = initial temperature of the flue gas.
t_f'' = final temperature of the flue gas.
Θ_i = temperature difference of the hot entering flue-gas and hot effluent oil.
Θ_f = temperature difference of cold incoming oil and cold exiting flue-gas.
Θ_m = mean temperature difference between the two fluids.
S_o = specific heat of the oil.
A = external hot area of heating surface.

$$\Theta_m = \frac{\Theta_i - \Theta_f}{\log_e \dfrac{\Theta_i}{\Theta_f}} = \frac{(t_i'' - t_f') - (t_f'' - t_i')}{\log_e \dfrac{(t_i'' - t_f')}{(t_f'' - t_i')}} =$$

$$\frac{(1700 - 400) - (650 - 118)}{\log_e \dfrac{(1700 - 400)}{(650 - 118)}} = \frac{768}{\log_e 2.44} = \frac{768.0}{0.892} = 861° \text{ F.}$$

Then:

$$H = \frac{W \times S_o \times (t_f' - t_i')}{A \times \Theta_m} = \frac{40{,}700 \times 0.45 \times 282}{14{,}000 \times 861} =$$

$= 0.43$ B.t.u. per hr. per 1° F. mean temperature difference.

It will be noted that in calculating H no account is taken of heat used in evaporating the volatil portions of the oil. If this were included in the numerator, and the difference in specific heat of oil and vapor taken into account, the value of H would be:

$$= \left\{\frac{[(6{,}105 \times 0.5) + (34{,}595 \times 0.45)] \times 282}{14{,}000 \times 861}\right\} + (18.75 \times 6{,}105)$$

$$= \frac{5{,}365{,}310}{12{,}054{,}000} = 0.446$$

The value of H is found to be only slightly different from that found in the first calculation in which the refinements were not taken into account. Furthermore it is difficult to say to what extent vaporization occurs in the pipe-still heating-coils. In all probability much of the vapor is formed after the oil enters the vaporizing tank, and at the expense of the heat content of the oil.

I have now digressed widely from the description of the plant, and must return to this at once. Figure 63 shows the pipe-still furnaces in more detail. The inspection and cleanout doors, the sampling pet-cocks, the 8-inch flow-line from the still to the vaporizing-chamber or "separator," the expansion-joint in the flow-line, the automatic temperature-control in 8-inch tee in flow-line, the steel-plate roofing, the buckstaying, and the breeching are all to be seen.

One of the oil-burners is shown in Figure 64. The manner of placing this burner is worthy of note. The small hole in the brick wall for the burner, and the damper controlling the air-supply are quite in contrast to the frequently observed method of sticking the burner through a hole two or three feet square with no control of the air supply.

The hot oil from the pipe-coils is discharged into a separating drum. The drums shown in Figure 65 are 10 feet in diameter and 16 feet 9 inches high. The oil passes over horizontal baffles to the bottom where a depth of 2 feet 4 inches is maintained. The horizontally placed equalizer-drum shown just to the right of the separator in Figure 65 is connected in such a manner as to control the level of the residuum in the separator.[22] The residuum is blown with steam in the separator, and then flows by gravity through the heat-exchangers to storage. It conforms in properties to the U. S. Standard Specification for Bunker Oil "C." The storage tanks are equipped with heating coils to keep the oil fluid so that it can be pumped to the tankers through the 10-inch submarine sea-loading lines. The discharge ends of these lines are moored about one mile from the shore.

The vapor passes from the top of the separator to dephlegmators shown in Figure 66. These are rectangular tanks built in three sections, with baffle plates and open-steam-coils in the bottom section, and cast-iron water-cooled coils in the top section. The extent of the condensation is controlled by regulating the cooling-water supply and by controlling the quantity of steam injected. A 62 to 66° Bé. gasoline distillate (130 to 440° F.), and a 54 to 60° Bé. (150 to 520° F.) distillate are thus separated in vapor form, and are condensed in the condenser seen in Figures 65 and 66. These distillates can be treated and re-run to produce finished products though this is not done at Tecomate.

The Griscom-Russell condenser equipment is used in the English refinery of the Atlantic Gulf Oil Corporation. The condensers at the Mexican refinery are of the box type, but fitted with "Vento" coils manufactured by the American Radiator Company. A Vento section

[22] The "separator" of the Lederer plant should not be confused with the "separator" of the Trumble plant. The former corresponds to the "evaporator" of the Trumble plant.

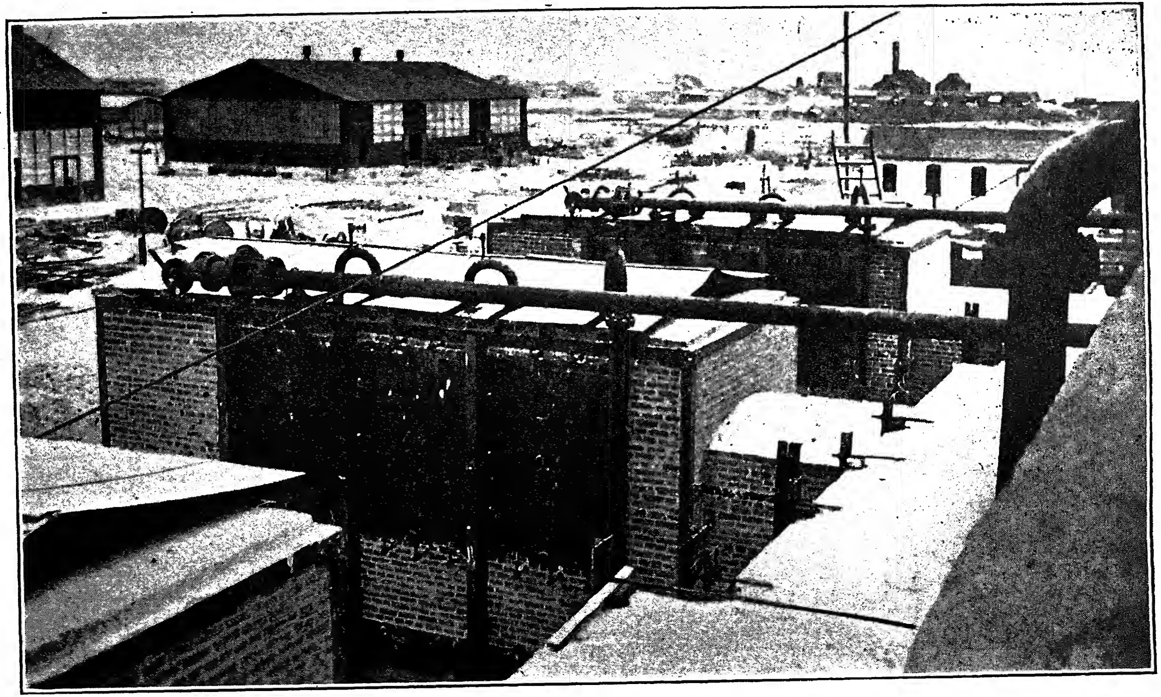


FIG. 63.—Pipe-Stills, Lederer Plant of Atlantic Gulf Oil Company.

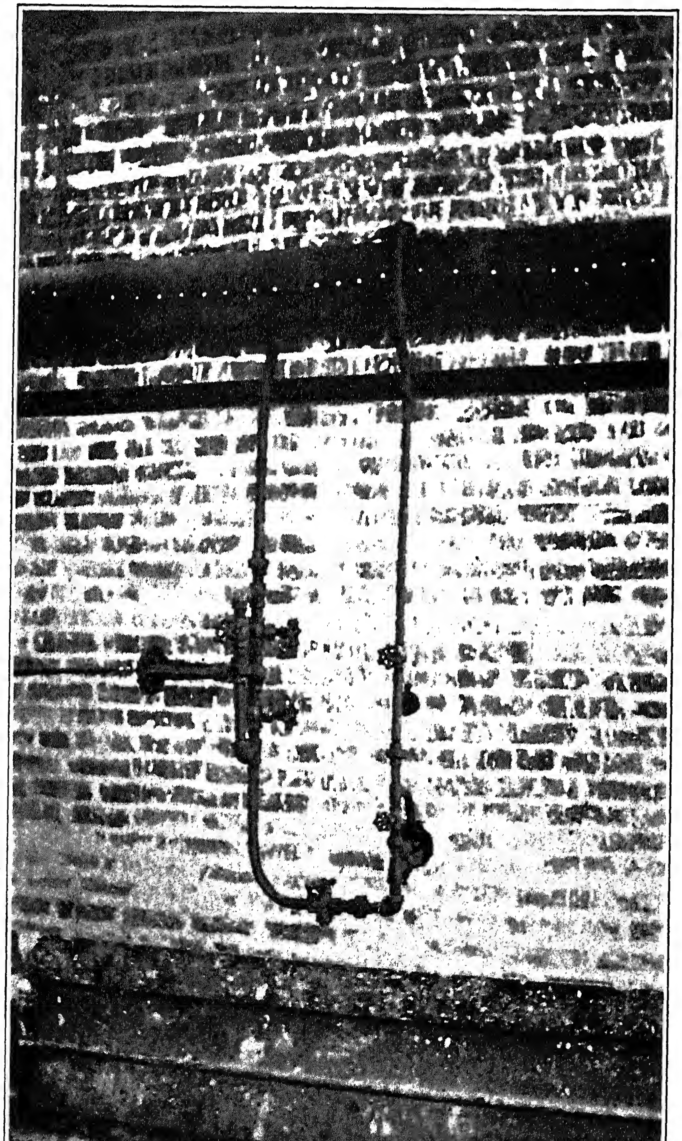


FIG. 64.—Oil Burner and Damper, Lederer Plant.

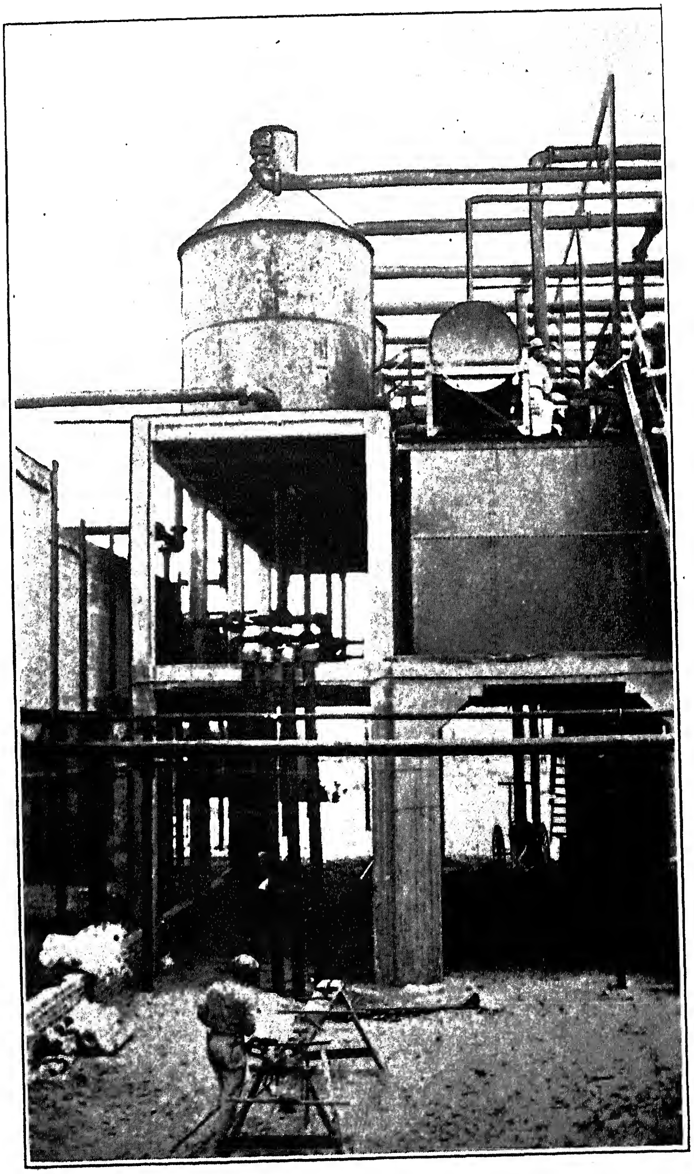


FIG. 65.—Separators, Vapor-Lines, Equalizer-Drums, and Condensers, Lederer Plant.

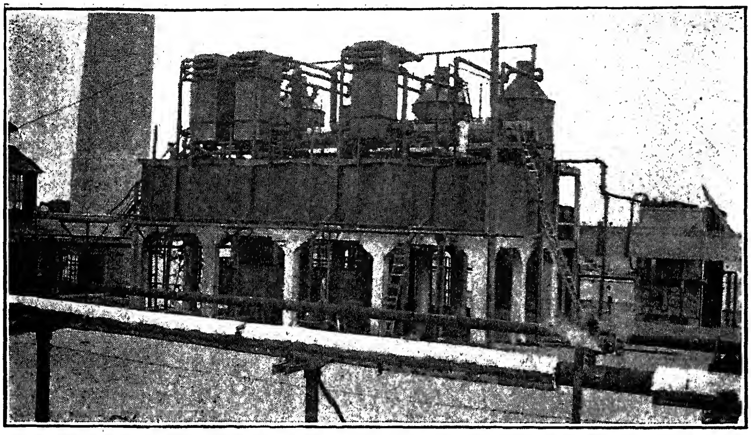


FIG. 66.—Dephlegmators and Condensers, Lederer Plant.

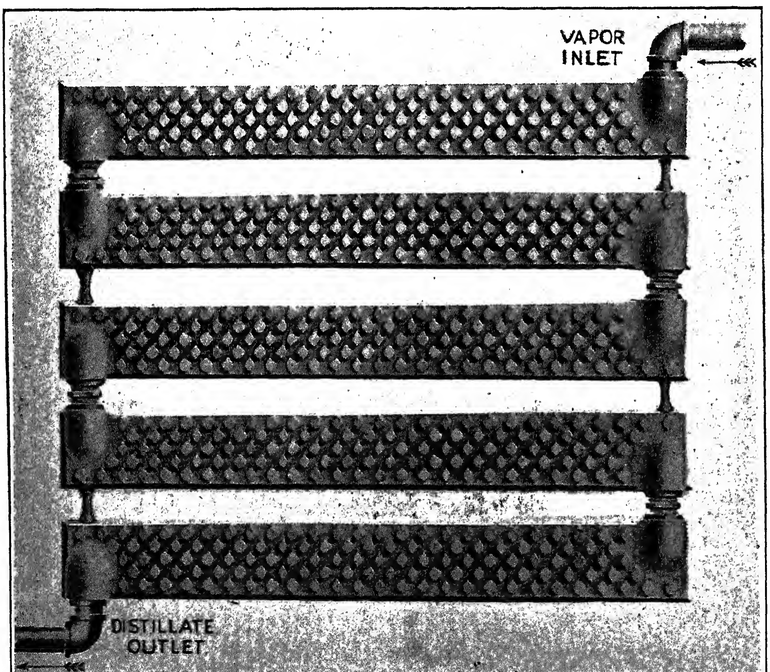


FIG. 67.—"Vento" Condenser Sections.

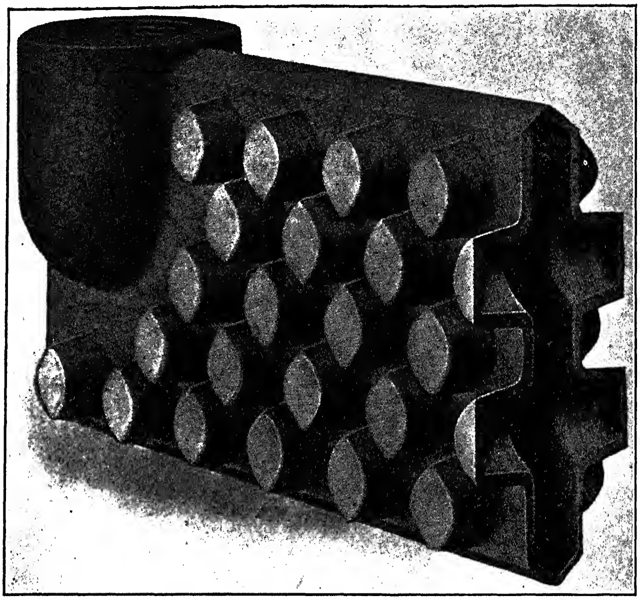


FIG. 68.—Cut-Away View, "Vento" Condenser Section.

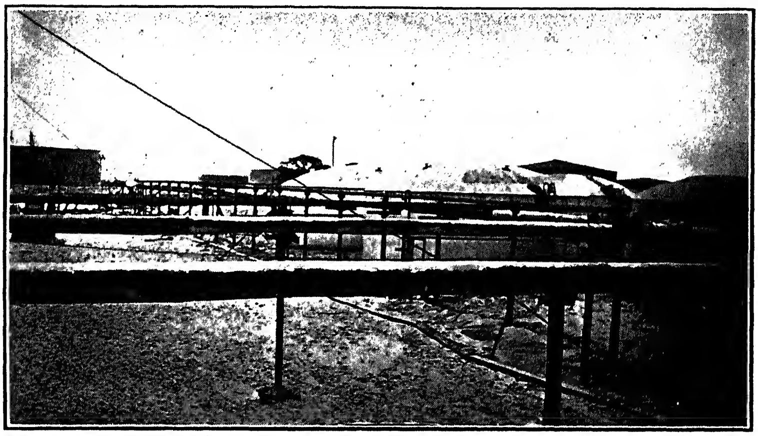


FIG. 69.—View of Yard Showing Steam and Air Lines and Run-Down Tanks at Tecomate.

is shown in Figure 67, and a cut-away view of a Vento unit is Figure 68.

The Vento is quickly and cheaply transported and erected. It offers a large cooling surface per unit of volume in a condenser box. The size and weight of the condenser box was 30 per cent less at the Tecomate refinery than an ordinary pipe-coil condenser of the same capacity. Broken or leaky condensing units are easily replaced. These advantages were of special moment in the construction of the plant at Tecomate because of the expense and difficulty of transporting materials.

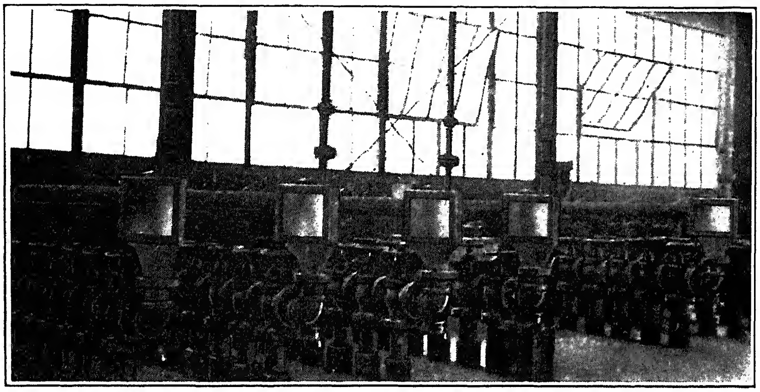


FIG. 70.—Receiving-House, Lederer Plant, Showing Look-Boxes and Manifolds.

Figure 69 shows the yard steam and air lines, and also part of the run-down tanks of the Mexican plant. The lock-boxes and manifolds of the receiving-house are shown in Figure 70.

The plant at Fawley, England, differs in many respects from the Tecomate refinery. An elevation, partly in section of the equipment at Fawley, is shown in Figure 71. The separator is cylindrical in form and supported directly above the furnace. It is really a still. The bottom is exposed to the hot flue-gas. Griscom-Russell condensing equipment is used.

Estimated Cost of a 42,000-Barrel Plant.

The following is an estimate of the cost of building a Lederer topping plant of 42,000-barrel daily capacity in Mexico. The data are based on June-July, 1921, prices of material, labor, and transportation.

LAND INVESTMENT (Oro National)		$250,000.00
STILLS:		
14 pipe stills at $50,400	$705,600.00	
Pipes, fittings, etc.	28,800.00	
2 Exchangers, complete	24,000.00	
Pumping equipment	48,000.00	806,400.00

Boiler House:		
1000 HP. (150% overload). Buildings	$52,800.00	
4-250 H.P. boilers in place	120,000.00	
Breeching	9,600.00	
Brick chimneys	19,200.00	
Steam lines	24,000.00	
Insulation	4,800.00	
Economizer	60,000.00	
Pumps, instruments, etc.	14,400.00	$304,800.00
Pump House:		
Building	28,800.00	
4 Circulation and Fire Pumps	19,200.00	
3 Distillate transfer pumps	7,200.00	
3 " loading "	9,600.00	
3 Fuel oil loading pumps	12,000.00	
2 Compressors	19,200.00	96,000.00
Tanks:		
10 Distillate Receiving Tanks 10 x 30	52,800.00	
4 37,500 bbl. tanks @ $60,000	240,000.00	
7 55,000 " " @ 70,000	490,000.00	
1 5,000 " fuel tank	24,000.00	
1 5,000 " water "	16,800.00	
Fire walls, etc.	48,000.00	
1 Auxil. cooling tank for hot fuel oil	19,200.00	890,800.00
Lines:		
Fire lines	112,500.00	
Water circulating lines	50,000.00	
Sewerage and drainage	25,000.00	
Pumping lines, loading lines, etc.	200,000.00	387,500.00
Buildings:		
Office buildings	28,800.00	
Fence	48,000.00	
Laboratory	19,200.00	
Foamite protection	192,000.00	
Shops	72,000.00	
Warehouse	28,800.00	
Houses for employees	144,000.00	532,800.00
Total for Land, Buildings and Equipment		3,268,300.00
Other Costs:		
Labor	1,100,000.00	
Engineering	326,830.00	
15 Per Cent Overhead	490,245.00	
15 Per Cent Extras	490,245.00	
Freight on Material	400,000.00	2,807,320.00
Grand Total		$6,075,620.00

Estimated Operating Costs and Profit.

The following is the estimated operating cost and profit of the e plant:

OPERATING COSTS:

Monthly payroll	$24,000.00	
Labor	3,000.00	
Fuel and steam	48,000.00	
Maintenance and repair	6,000.00	
Electric power	2,000.00	
		$ 103,000.00
1. Operating expenses per year $103,000.00 x 12	1,236,000.00	
2. 6 per cent interest on investment $6,075,620.00	364,537.20	
Interest on working capital $800,000.00 @ 6 per cent	48,000.00	
3. Insurance @ 1.00 per $100 buildings and stored oil $6,000,000	60,000.00	
4. Depreciation 15 per cent per year	911,343.00	
5. Overhead expense	480,000.00	
		3,099,880.20
Running expense per 12,600,000 barrels (300 days per year)	$3,099,880.20	
Running expense per barrel	$0.246	

ESTIMATION OF PROFIT:

Crude oil market	$1.60 per bbl.	
Fuel oil market	1.75 " "	
Distillate market	4.00 " "	
1 barrel crude @ 21.5° Bé		$1.60
Cost of refining		.246
.70 barrels fuel at $1.75	$1.225	
.16 barrels distillate @ $4.00	.64	
Profit per barrel of crude		.019
	$1,865	$1,865

Comparative Merits of Pipe-still and Ordinary Crude-still.

The statement is often made that the ordinary cylindrical crude-still bears the same relationship to the well designed pipe-still as the tea-kettle does to the modern water-tube boiler. This comparison gives an exaggerated impression of the merits and usefulness of the pipe-still in the present state of development of this type of skimming or topping apparatus.

The cylindrical still can be used for topping, running to coke, steam distillations,—in fact for all types of distillation. It is a most inefficient apparatus for any single purpose, but the fact remains that it possesses this general utility. The small refiner who must have a very flexible plant will probably cling to the conventional still. The pipe-still on the other hand is a specialized apparatus. The pipe-still and its dephlegmating and condensing equipment are particularly adapted to handling large daily runs of fairly uniform crude oil, though a reasonable flexibility is to be had without difficulty. The pipe-still plant can be built for small capacity if it is to be used for the simpler topping operations, but in its elaborated and refined design it is distinctly a plant for the large company.

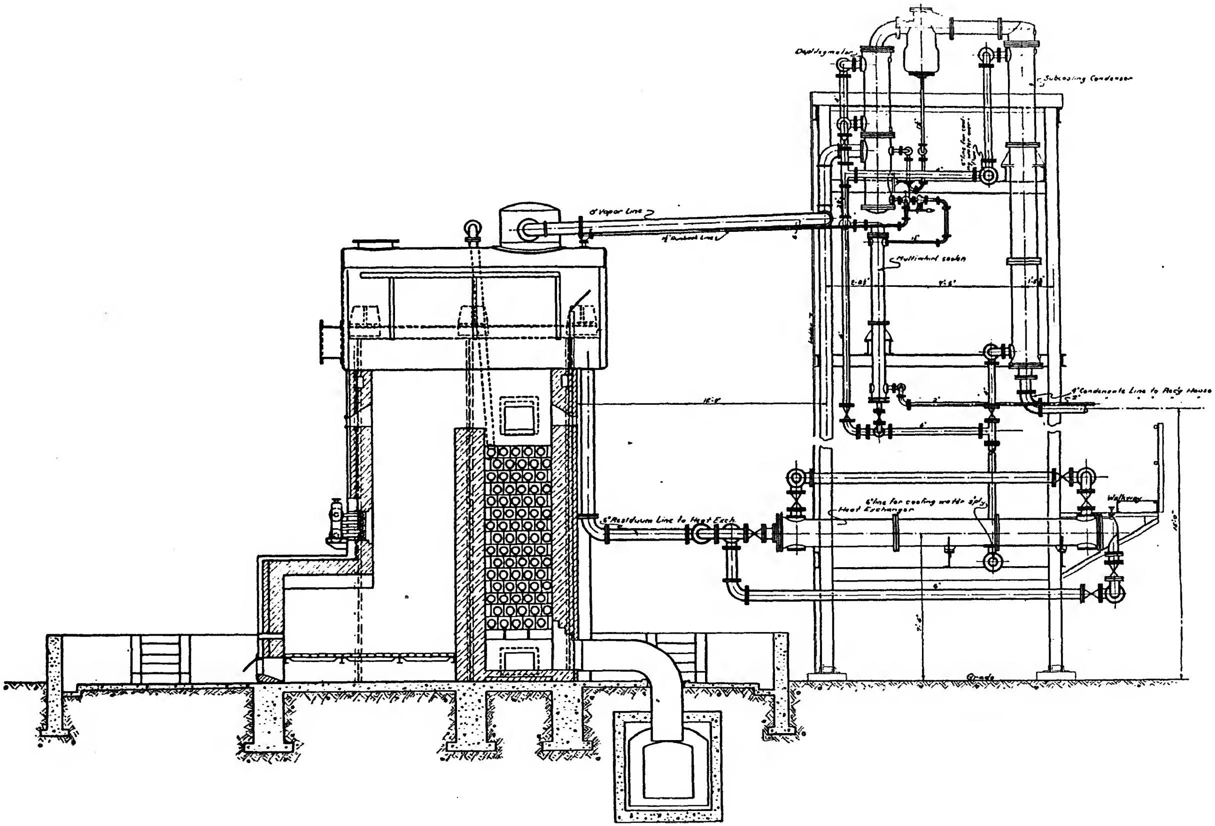


FIG. 71.—Topping Plant of Atlantic Gulf Oil Co. at Fawley, England.

The pipe-still contains little oil at any one time, whereas the crude-still contains a large volume. The oil flowing through the pipe-still is evenly heated if the velocity of flow exceeds the critical velocity. The oil in a cylindrical still is not uniformly heated, but is overheated near the shell of the still. This cannot be entirely prevented by agitation with steam. The oil is decomposed to some extent, and carbonaceous deposits are formed on the still-bottom. The formation of deposits is greater when the oil contains salt-water, grit and sand.

As a general rule pipe-still furnaces have been more intelligently designed than the furnaces beneath ordinary stills, and for this reason the fuel consumption of the ordinary still-plant is often two or three times that of the pipe-still plant. The fuel consumption of the pipe-still plant can be reduced to 1.0 per cent of the oil run, even when as much as 25 per cent of the oil is evaporated. However, the fuel consumption of a well-designed battery of conventional stills when run as a continuous plant is little higher than that of pipe-still plants of current design. This is shown by the data of Table XLVIII.[23] The battery of conventional stills used only 1.1 per cent fuel in removing 24.1 per cent of tops, as compared to a consumption of 1.1 per cent fuel for removing 18.4 per cent of tops in the Martinez Trumble plants. The Coalinga Trumble plant used 0.88 per cent fuel in removing 21.5 per cent of tops. However, when the fuel requirements for re-running and generation of steam are taken into account, the better over-all economy of the pipe-still and adjunct apparatus is seen. These data are given in Table XLIX. The per cent of tops removed in each plant is different and this must be taken into account.

In the event of a fire the pipe-still possesses the advantage that only a small volume of oil is contained in the still. The danger of a disastrous fire is minimized, but fires are not at all impossible. If the oil contains salt water and grit, freakish pitting of parts of the circulating system may occur. At Vernon the upper ell, in the riser through which the oil was discharged into the evaporator, pitted badly. This difficulty could of course be overcome by the use of fittings made from special alloys.

The pipe-still leaks less frequently than the cylindrical still, and leaks are more easily handled. In general the pipe-still is easier to keep in repair. If the still is properly operated, deposition of carbon will be negligible, but should deposits form they are easily removed without loss of time in cooling and ventilating the still as is necessary in cleaning the conventional type of still.

Crude oils containing water are more easily handled in pipe-stills than in ordinary stills. In fact the pipe-still if used in conjunction with a properly designed separating chamber is an excellent dehydrator. This is of special importance in the treatment of heavy asphaltic oils.

The first cost of a pipe-still plant for a given capacity is much less than that of a still plant. Table XLIX[24] shows the cost, per barrel

[23] *Bull. No. 162,* U. S. Bur. of Min., p. 153.
[24] *Bull. No. 162,* U. S. Bur. of Min., p. 154.

TABLE XLVIII

SUMMARY OF TOPPING PLANT RECORDS SHOWING FUEL CONSUMPTION AND PRODUCTS

Name of Plant	Average Per Month											
	Gross Barrels of Crude Run	"Tops" Made		Water Dehydrated[a]		Residuum Made		Refining Loss		Fuel Consumed Under Stills	
		Barrels	%	*Barrels*	%	*Barrels*	%	*Barrels*	%	*Barrels*	%
Conventional stills[b]	401,853	96,690	24.1	......	.....	300,890	74.8	2,206.4	0.55	4,508	1.1
A. F. L. Bell	186,971	42,250	24.1	5,609	3	139,000	74.8	1,082	.55	2,087	1.6
Brea plant	169,330	26,300	15.5	5,210	3.08	135,000	79.8	2,823	1.67	......	....
I. W. Fuqua	239,708	26,294	11	......	.....	....	....	....	....	......	1.6
E. I. Dyer	228,955	32,340	14.2	46,638	20.7	138,766	60.5	1,608	.70	None	....
Brown-Pickering.	87,000	5,250	6	15,750	18	66,000	75.9	....	....	......	....
Prutzman	55,860	14,167	25.4	6,670	12	32,160	57.8	1,400	2.5	......	....
Fellows Trumble .	151,978	17,940	11.8	......	.....	....	....	6,380	4.2	1,400	.92
Vernon Trumble .	305,205	25,900	8.5	......	.....	....	....	....	....	2,524	.90
Coalinga Trumble	57,925	12,450	21.5	......	.....	45,126	77.9	318	.55	5,100	.88
Martinez Nos. 1 & 2	434,882	114,800	18.4	......	.....	350,658	80.5	4,100	.94	4,780	1.1
Total	2,319,667	417,381	18	......	.....	1,207,600	....	21,300.4	.86	21,290	....
Average	....	....	....	......	.....	....	....	....	....	......	0.92

[a] Records of water dehydrated were not available for all plants.
[b] The continuous conventional still plant described in the first part of this chapter.

of capacity, of several plants. Other comparative data are given as well. The cost data are based on pre-war prices and are not representative of present costs.

Comparisons of plants must take into account local conditions, and requirements for these often determine the type of plant best fitted to do the work. The problems of construction and operation must be carefully studied in each instance in order to insure satisfaction and economy.

The important developments that are to come will be concerned not so much with the pipe-still itself, but with the apparatus in which vaporization and separation into various fractions occur. This is where fundamental principles have been overlooked or violated in design, and where improvement holds forth the reward of greater flexibility and economy. I shall recur to this subject in the next chapter.

TABLE XLIX

TOPPING PLANT OPERATING DATA

Name of Plant	Computed Percentage of Fuel Consumed Under Boilers per Barrel of Crude Oil Run	Percentage of Fuel Used in Re-running per Barrel of Crude Oil Run	Total Percentage of Fuel Used per Barrel of Crude Oil Run	Boiler Horse Power of Steam per Barrel of Tops	Barrels of Cooling Water Used per Barrel of Tops Made	Cost of Plant per Barrel of Daily Capacity
Conventional stills[b]	0.88	0.23	2.13	4.1	14.0	$16.80
A. F. L. Bell	0.55	0.23	2.38	2.8	14.0	12.80
Brea	....	....	....	....	....	......
I .W. Fuqua	0.50[a]	0.15[a]	2.25	....	12.5	7.00
E. I. Dyer	....	....	....	....	20.7	28.55
Brown-Pickering	....	....	....	....	....	......
Prutzman	....	....	....	....	....	......
Fellows Trumble	....	....	....	....	....	2.00
Vernon Trumble	0.24	....	1.14	3.0	....	5.80
Coalinga Trumble	0.19[a]	....	1.07	....	15.0	7.48
Martinez Trumble Nos. 1 and 2	0.12	....	1.23	0.72	20.7	8.5
Average	....	....	2.01	....	....	......

[a] Figures estimated.

[b] The continuous conventional still plant described in the first part of this chapter.

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Chapter VII.

Towers, Dephlegmators, Steam-Stills, Condensers, Heat-Exchangers, Coolers, and Other Refinery Equipment.

Towers, dephlegmators, steam-stills, condensers, heat-exchangers, and coolers are apparatus of the greatest importance in every refinery. My purpose is not only to present information and suggestions that may be of assistance in designing and using these apparatus, and in selecting the proper equipment for securing a particular result, but more particularly to evoke critical study and analysis of apparatus now in use.

To illustrate the application of fundamental principles in the design of fractionating apparatus, I have chosen to discuss the Trumble process. I trust that my motives in this matter will not be misinterpreted. I have no desire to be critical for criticism's sake, but I am convinced that critical study is a necessary precedent to real progress. I have limited my discussion to a few apparatus, for to describe and analyze more than a few of the hundreds of different kinds that have been used would be to lose my main purpose in a mass of detail.

The Trumble process lends itself to my purpose for several reasons. It is well known to the industry, and is now recognized as being applicable not only to topping, but to the accomplishment of a wide variety of purposes. It affords me an opportunity to illustrate the point that fairly general acceptance of a process is not necessarily a guarantee that it is fundamentally correct. In matters of layout and external appearance the Trumble plant leaves little to be desired. The galaxy of dephlegmators, separators, condensers, exchangers, piping, and valves is most impressive. Were the process as sound in its fundamentals, and were the several apparatus as correct fashionings in iron and steel, of basic principles, as the plant is impressive in its outward aspects, I should have been forced to seek further for an example to illustrate my discussion.

By way of further introduction may I make it clear that I do not wish to convey the impression that the Trumble process is not effective. Not only are separations effectively made, but the process is of better than average efficiency. But I trust it will be clear that the same work can be done as effectively, and more efficiently, by means of apparatus that is less complicated and far less costly.

I do not wish to belittle the valuable services of Mr. Trumble and those who with him blazed the trail in the development of the process. It is easy to criticise, not so easy to create. Knowledge of distillation and dephlegmation now available, and which was not in existence a few years ago, makes the design of apparatus for the distillation of petroleum a far easier matter than formerly.

In fairness to myself, and lest I be accused of criticising destructively without constructive suggestion, I must confess that on account of patent matters I do not feel it advisable to express myself in a constructive way as freely as I should like.

The Trumble pipe-still has been described in Chapter VI. This part of the Trumble plant is efficient and correct in principle. The design of the heating-coils may be refined and improved somewhat, as has been done by the Power Specialty Company, but in general, this will be refinement and not radical change. I am not concerned with this.

The tubular condensers, coolers, and heat-exchangers of the Trumble plant are described in the latter part of this chapter. Comparison with other designs and types also described there suffices for these apparatus. In general it will be noted that there is room for improvement in design along lines similar to those followed by the Griscom-Russell Company, the Hope Engineering and Supply Company, the American Radiator Company, and others.

The Trumble Process in Brief.

The Trumble process has been described in Chapter VI. It will be recalled that it consists in pumping the crude oil through heat-exchangers countercurrent to the hot residuum, then through a pipe-coil heater in which the temperature is raised to any required degree, and then discharging the heated oil into a chamber in which a vapor is flashed from the liquid. The residuum is used as a heating medium in the separators. The vapor passes through a series of dephlegmators in each of which a part is condensed. The vapor from the last dephlegmator is condensed, and is of course the lightest fraction. The liquids condensed in the dephlegmators may be run through coolers to the run-down tanks, or may be run through the "separators" or continuous steam-stills in order to separate them into two or more fractions. Vapors from the separators pass to condensers, and the liquids through coolers.

For the moment, I shall assume that the general scheme of the Trumble process is fundamentally correct, and shall proceed to consider the merits of the evaporator, the dephlegmator, and the separators as apparatus for the accomplishment of the particular result desired.

The Trumble Evaporator.

The Trumble evaporator has been shown in Figure 56. The purpose of this apparatus is to flash a vapor from the heated crude in such

a manner as to effect a clean-cut separation, and also to utilize some of the heat in the flue-gas from the pipe-still furnaces. Liquid droplets should not be entrained in the vapor. Let us see how well the evaporator fills the bill.

I have shown in Chapter IV that the column is an effective and the most efficient apparatus for separating substance A from a mixture of substances A and B. It is likewise the best apparatus for separating a vapor containing both A and B from a liquid containing A and B, and analogously for separating a vapor composed of several volatil hydrocarbons from a liquid containing these as well as less volatil hydrocarbons. The excellent effectiveness and the efficiency of a column apparatus for accomplishing these separations is the result of the establishment of a succession of near-equilibria between vapor and liquid. This can only be done in an apparatus whose mechanical features provide for continuity of contact of vapor and liquid from one end of the apparatus to the other, and at the same time for sample contacting surface. However, the Trumble evaporator is not expected to produce a change in composition of vapor and liquid after these have been formed. That is, the apparatus is not expected to produce a result that could be obtained by the use of a number of column-sections. Rather it is expected to approximate to the result obtainable by the use of a *single* perfect-section, that is, the establishment of equilibrium between vapor and liquid. Actual equilibrium between vapor and liquid is the limiting result.

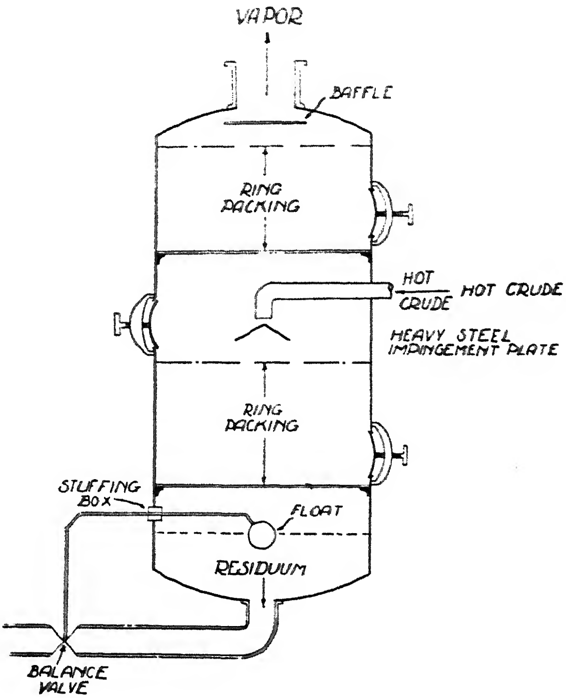


FIG. 72.—Leslie-Baker Vaporizer.

The Trumble evaporator accomplishes the desired result fairly well, but it is an unnecessarily large and expensive piece of equipment.

Also entrainment occurs, and either makes necessary the use of a baffled trap, or results in unnecessary inclusion of residuum in the condensate from the first dephlegmator.

The desired results can be better accomplished, and a considerable saving in first cost of equipment can be made by use of an apparatus [1] such as that shown diagrammatically in Figure 72. The hot crude oil enters as indicated, impinging on a heavy steel cone, then flows downward and spreads over the surfaces of the packing. Ample opportunity is thus afforded for clean-cut separation of liquid and vapor. The vapor passes upwards through another layer of packing where entrained liquid droplets are scrubbed out. Mechanical features are indicated in the diagram and need no comment.

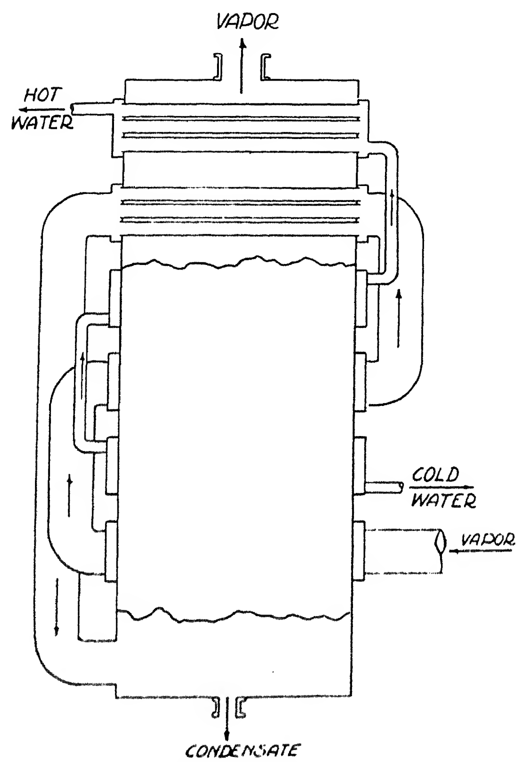


FIG. 73.—Diagrammatic Showing of the Trumble Dephlegmator Used by the General Petroleum Corporation.

The apparatus shown in Figure 72 would not be mounted in the stack of the pipe-still, but would be located conveniently, and would be well lagged to avoid heat loss. The temperature of the flue-gases from the pipe-still should be reduced as far as economical by passage over preheated coils or sections. If the crude is rich in volatil fractions it should be heated by passage through the exchangers and preheater-coils in the last pass of the pipe-still, and then discharged into a flash-vaporizer similar to that shown in Figure 72. The residuum from this vaporizer should be heated in the pipe-still and discharged into a second flash-vaporizer. The removal of the lightest vapors in the first vaporizer eliminates liberation of gas and formation of light vapors in the pipe-coil heater, and by so doing increases the rate of heat-transfer in the heater. It

[1] Application for U. S. Letters Patent on apparatus of this type has been filed.

should be recalled that gas films offer high resistance to the flow of heat.

The Trumble Dephlegmators.

Several types of dephlegmators have been used in Trumble plants, but I shall confine my discussion to a type used by the General Petroleum Corporation and to another used by the Shell Company. The dephlegmator used by the General Petroleum Company is shown diagrammatically in Figure 73. It consists of a rectangular steel shell 4′ x 6′ x 16′ with six banks of 2-in. boiler-tubes. The vapor passes through three of the banks of tubes as indicated, and then enters the bottom of the dephlegmator. The other three banks of tubes are water-cooled.

The vapor entering the bottom of the dephlegmator passes a hot tube-bank and then strikes a cold tube-bank where a part of it is condensed. The condensate formed in this manner drops onto the hot tubes below, where a part is re-vaporized. The other tube-banks function in a similar manner. This type of dephlegmator is apparently the result of the following general line of reasoning:

> "In simple fractional distillation the vapor is composed of more volatile substances than the liquid. If the vapor is condensed and redistilled a vapor still more volatile is obtained, and so on. But dephlegmation is the inverse of simple distillation, and therefore can be effectively accomplished by a succession of condensations. Experience teaches, however, that as a result of the imperfections of the process the condensates contain volatile as well as the less volatile components, and must therefore be reheated to some extent. This can be accomplished by placing a bank of hot tubes beneath each bank of cold tubes."

Before commenting on this dephlegmator I wish to recall from the subject matter of Chapter IV that there are two limiting types of dephlegmators, first the "simple" dephlegmator, and second the "differential" dephlegmator. Any apparatus in which liquid and vapor are brought into intimate contact at a *fixed* temperature will in operation approximate the results obtainable by use of a simple dephlegmator. Any apparatus in which temperature is free to vary with composition of vapor and liquid and in which the condensate is removed as rapidly as possible from all parts of the apparatus will in operation approximate the results obtainable by differential dephlegmation. We have seen that simple condensation is the least efficient means of fractionation, and that differential dephlegmation, although far more efficient than simple condensation, is much less efficient than distillation through a column. This of course raises the question as to whether dephlegmators should ever be used. I shall hold my answer to this in abeyance for the moment, but shall recur to this subject shortly.

The Trumble dephlegmator shown in Figure 73 is open to criticism on several grounds. The tendency of a bank of cold tubes is to cool both liquid and vapor to a temperature that approximates the tempera-

ture of the tubes themselves. The more intimate the contact of vapor and liquid under these circumstances the more nearly does the result approach that of the inefficient simple dephlegmator. The presence of the hot tubes doubtless causes some revaporization, but also nullifies in some measure the cooling effect of the cold tubes. The use of alternate banks of hot and cold tubes is the result of a rather crude mechanistic conception of the process of change in composition. Discontinuity of conditions exists rather than the continuity necessary to the easy accomplishment of the desired result.

A further and important defect of the Trumble dephlegmator is that no provision is made to remove the liquid as soon as it is formed.

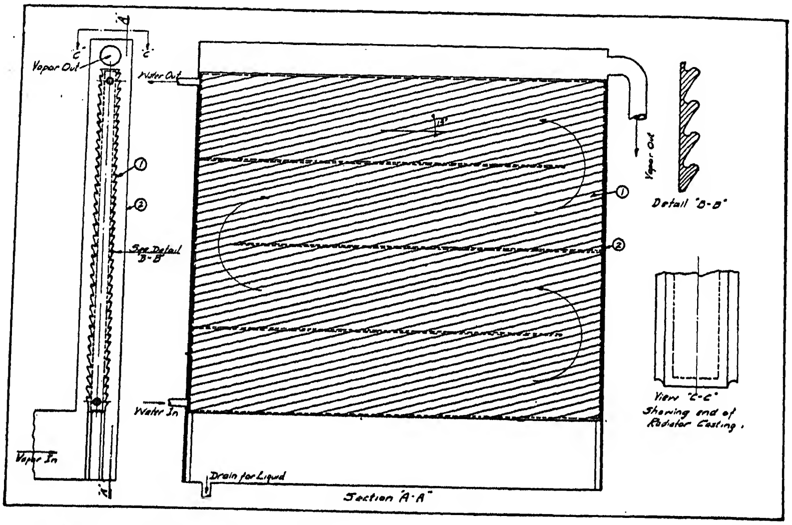


FIG. 74.—One Type of Leslie-Baker Differential Dephlegmator.

This is provided for in an effective manner in designing the dephlegmator,[2] one unit of which is shown in Figure 74. The vapor ascends along a casting whose surfaces are ribbed or channeled as indicated. T·quid is formed on the surface of the casting, but, as soon as formed, ···ns downward and is caught in the channel just below. The chan- ᶦope downwardly, at an angle of 15°, across the surface of the Thus, the liquids are conducted to one side, and out of contact vapor, almost as soon as they are formed. The process of .l condensation is not truly differential, but approximates to the)f differential condensation. That is, a small weight of liquid l, and conducted away as soon as formed. The enriched vapor nward. More liquid is formed from the enriched vapor, and

lication for U. S. Letters Patent on apparatus of this general type filed.

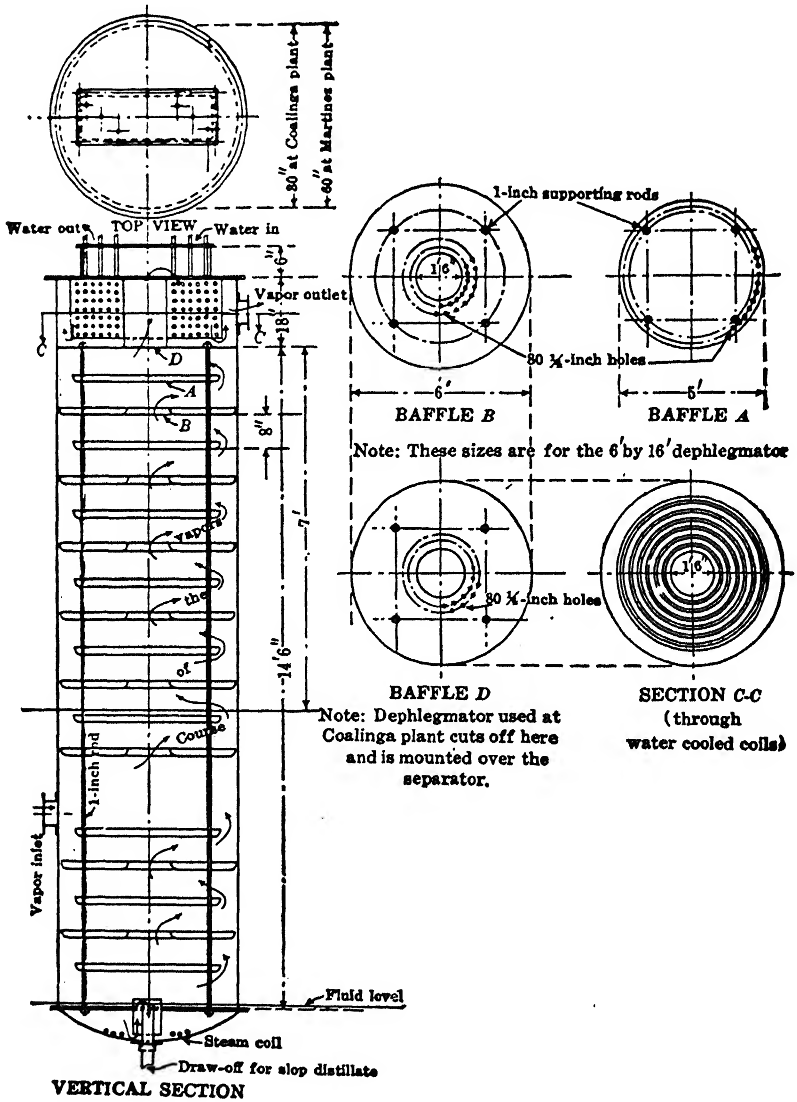


FIG. 75.—Trumble Dephlegmator Used by the Shell Company.

quickly conducted away. And so, through a repetition of this process, a highly satisfactory enrichment is accomplished. Cooling water flows through the baffled passages inside the casting. The unit construction is desirable from the standpoint of flexibility, both of design and capacity. Any number of the dephlegmating units can be combined into a single dephlegmator in any desired manner.

The Shell Company's Trumble Dephlegmator.

The Trumble dephlegmator shown in Figure 75 and used by the Shell Company is a more efficient apparatus than that used by the General Petroleum Corporation. It consists of a steel cylinder within which is a series of circular baffles. A limited condensing surface is provided at the top, and a small steam coil in the bottom. This apparatus is an improved form of the baffled dephlegmator that depends for its cooling on the heat conductance of the baffles, and heat loss from the external surface. However, vapor and liquid are not brought into intimate contact, and for this reason the change in composition of liquid and vapor is small when the size of the apparatus is considered. The Shell-Trumble dephlegmator (Pyzel, U. S. Patent 1,276,690, Aug. 20, 1918) appears to be a "literal" translation into American engineering practice of von Niekrass' dephlegmator, patented in Austria in 1904 (Austrian Patent 16,954), and described in "Das Erdöl," volume III, page 312.

A small apparatus of the type shown in Figure 76, and which I shall next discuss, will accomplish as much as a far larger Trumble-Shell dephlegmator. Nevertheless, the Trumble-Shell dephlegmator is far more effective than the majority of those now in use.

Should Dephlegmators Be Used for Fractionation? If Not, What?

The purpose of dephlegmation is sharply to separate a vapor into a vapor containing the desired volatil components and a liquid containing heavier components. My answer to the question "Should dephlegmators be used?" is, in general, in the negative. I am not of the opinion that they should never be used, but I am convinced that in nine cases out of ten in which dephlegmators are used they could be replaced with other apparatus of lower first-cost, and of better operating efficiency, and therefore of lower operating-cost. In support of this statement I present Figure 76 which represents in a purely diagrammatic way an apparatus than can with profit replace most dephlegmators.

This apparatus [3] is an assemblage of sections, each of which contains a shelf carrying a number of nipples through which liquid overflows to the section below, and through which vapor rises to the section

[3] Application for U. S. Letters Patent has been filed on a fractionation process and apparatus of this type.

above. Each section is filled with an effective tower-packing or consists of any other well-known means of contacting liquids and vapors. Vapor enters the bottom of the apparatus as indicated, and in its upward flow meets liquid descending. Except for such convective cooling as is unavoidable, no heat is lost in the fractionator. The entire apparatus is well lagged. Vapor leaves the top of the fractionator and enters a condenser of any preferred type. The entire vapor, or any desired or required part of the vapor, is condensed and returned to the top section of the column. Provision is made to remove liquid from each section of the apparatus, although liquid may be removed only from a few sections, or, if it is desired to separate only into a volatil product and a less volatil residuum, liquids will be withdrawn only from one of the top sections and from the bottom of the fractionator.

As many sections as desired may be included in the apparatus. The compositions of vapor and liquid vary continuously from one end of the apparatus to the other. Hence a number of "cuts," or liquids of different composition, can be drawn from the sections. It should be recalled that the rate of change of composition of vapor and liquid in a column apparatus is a function of the weight of refluxed liquid, that is, of the weight of liquid running down the column. Hence the quantity of liquid removed from the upper sections will determine the performance of all sections below. In practice it will be desired to obtain some particular result. This can easily be done by removing liquid from selected sections in amounts determined by the performance requirements.

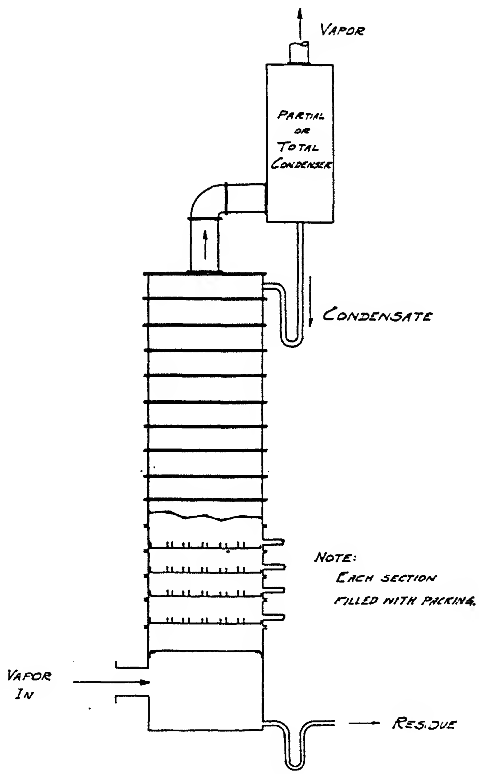


FIG. 76.—Leslie-Baker Fractionator.

This apparatus and process of dephlegmation and fractionation are of the widest application. After I have described the Trumble "separator" or continuous steam-still, I shall return to the apparatus I have

just described and show how it can be made a part of what I consider the most efficient and economical process and apparatus for distilling petroleum.

The Trumble Separator.

The Trumble separator has been shown in Figure 57. The separator is used to "clean-up" the dephlegmator bottoms, that is, to remove the lighter hydrocarbons present in small to moderate quantity in the condensates formed in any dephlegmator. The liquid enters one of the lower chambers of the separator, filling it to a depth of about 12 inches, and flowing through three or six of the chambers in series. Heat is transferred to the liquid from six 2-inch boiler tubes in the lower part of each chamber. The tubes are heated either by hot vapors or hot residuum. Steam is introduced from a perforated pipe several inches beneath the surface of the liquid in each compartment. The vapor passes upward through thimbles into an upper compartment from which it flows to a condenser. Liquid collects on the steel sheet that carries the thimbles and is heated somewhat by the vapors in their outward passage. The top of the separator is a pan that contains water. As a result of the cooling effect a small amount of vapor is condensed on the bottom of this water-cooled pan. However effective the separator may be as a tubular heater, it is a clumsy, expensive, and both ineffective and inefficient steam-still and fractionating device. Not only does theory show this, but it is tacitly admitted in practice for the vapors from the separators are passed through small dephlegmators to better the separation.

To use steam effectively in distillation it must be brought into intimate contact with liquid and vapor. To distill effectively, opportunity must be given for intimate contact of liquid and vapor, and for successive and continuous change in composition. The design of the Trumble separator does not take these fundamental principles into account.

The removal of the more volatil portion of the liquids condensed in the Trumble dephlegmators can be easily effected in a continuous steaming-column whose cost would be only a fraction of that of a separator, and which would occupy far less space. Steam is necessary because the residuum or vapors used for heating are not hot enough [illegible] the temperature and vapor-pressure of the bottoms sufficiently [illegible] of fractionation without steam. By using steam to equalize [illegible] of the pressure of the atmosphere the desired fractionation is easily made in a continuous steam exhausting-column.[4] The discussion of steam distillation theory in Chapter IV, and of steam-still equipment in this chapter, will be found of interest in this connection.

[4] Application has been filed for U. S. Letters Patent covering a process of and apparatus for continuous steam exhaustion, applicable to perform work such as that done by the Trumble separator, to the reduction of oils to flash, to the reduction of lubricating stocks to viscosity, and for other similar purposes.

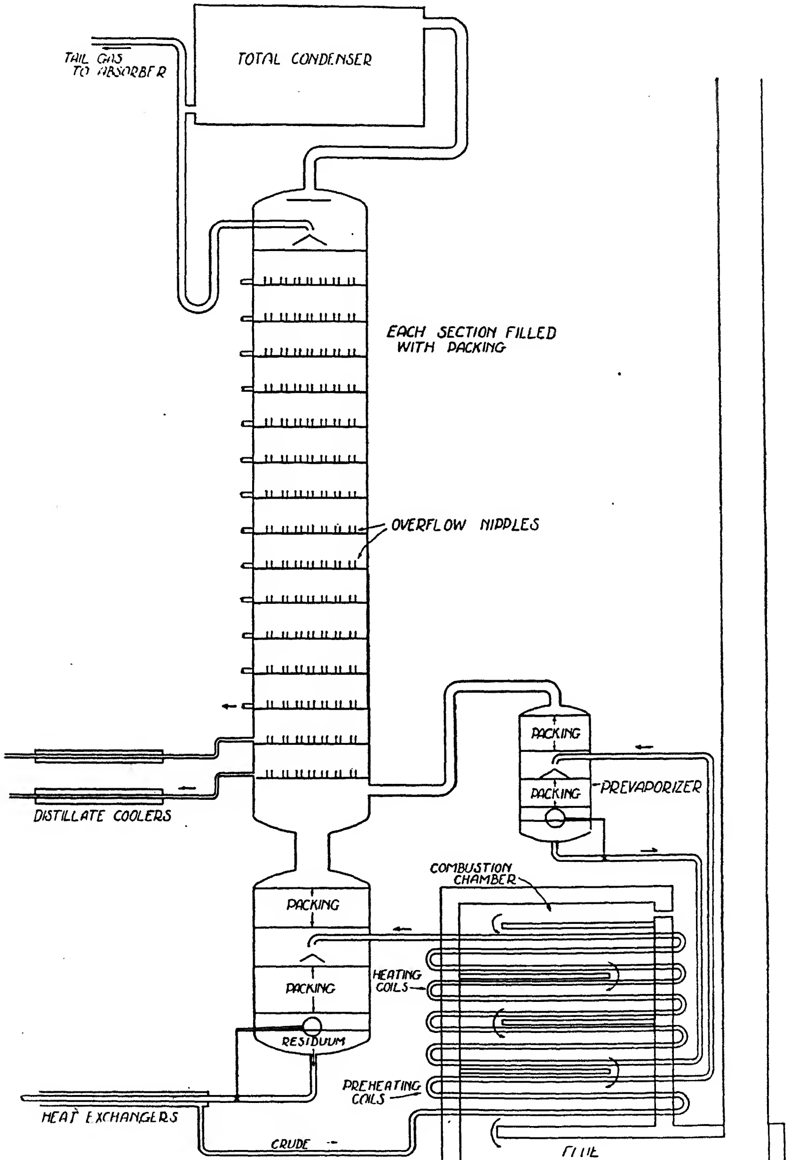


FIG. 77.—Leslie-Baker Plant for the Distillation of Petroleum.

The Leslie-Baker Process and Plant for Fractionating Petroleum.

I now wish to describe a process and apparatus [5] that in my opinion embodies the fundamental theory of fractional distillation as it should be applied to the separation of a number of fractions from crude petroleum or other hydrocarbon mixtures. Lest the reader be under misapprehension I wish to state that at the time of this writing this plant and process is not in use. I present it because I have been critical in my discussion of other apparatus, and feel that, valuable as criticism may be, it must be accompanied by constructive suggestion and effort. I shall not go into all the mechanical details of the apparatus, but shall content myself with presenting a diagrammatic representation of the apparatus in Figure 77. The indicated location of the several apparatus is not necessarily that which would be used in practice, but rather that which is convenient for diagrammatic presentation. Pumps are not shown. Pipe-still heater, heat-exchangers, coolers, and condenser can be any efficient type. Provision can be made if desired for recovery of the heat in the vapor, as well as that in the residuum.

In the light of the discussion in the foregoing pages the apparatus shown in Figure 77 needs very little explanation. The incoming crude is heated by out-going residuum, passes through preheater coils, and is discharged into a pre-vaporizer the design of which has already been discussed. Here the lightest vapor and any dissolved gas are separated and piped to join the main stream of vapor.

The residuum from the pre-vaporizer is passed through the pipe-still heater where it is heated to the required temperature, and then discharged into the main vaporizer. This apparatus, as well as the pre-vaporizer, can be built as an integral part of the fractionator if this is desired. The combined vapors from the pre-vaporizer and main vaporizer enter the bottom of the fractionator, or the light vapors from the pre-vaporizer may preferably be introduced into the fractionator at a point where they approximate to the composition of the vapor in the fractionator.

The principles on which the design and operation of the fractionator are based are the same as those discussed in relation to the apparatus shown in Figure 76. In fact the fractionator is simply a ·re apparatus of the same type. It provides for continuous change mposition of vapor and liquid throughout the apparatus. Either r liquid can be drawn from any or all sections, but in general more convenient and economical to withdraw liquid. All or he vapor leaving the top of the fractionator can be condensed and returned. The selection of the sections from which liquid is to be drawn, and the determination of the quantity to be drawn from each, is based on the products that are to be made. Liquids from the sections, separately or in any desired combination, flow through coolers

[5] Application for U. S. Letters Patent have been filed covering the process and apparatus described here in a general way.

and then to the running-tanks. The tail-gas from the condenser is scrubbed with one of the heavier naphtha fractions that is part of the gasoline stock.

The process and apparatus are exceedingly simple to operate. Heat losses are minimized because the two vaporizers and the fractionators combine all the functions of the numerous dephlegmators, separators and other fractionating equipment of other systems. Simplicity and heat economy result in low fuel, labor, and repair charges. For the same reason first cost is low. The functions of numerous dephlegmators, separators and other fractionating equipment of such processes as the Trumble are performed by vaporizers and the fractionator. In place of the large and costly piping and valves of the plant that handles the fractions in vapor form, we use the smaller piping and valves required for handling the fractions in liquid form. Not only is the size of the piping reduced but the total length of piping required is minimized. As a result of lower first cost the current charges for interest and depreciation are greatly reduced.

The apparatus that I have described is applicable not only to topping or skimming, but also to the distillation of heavy oils. Despite an apparent misapprehension, the use of a pipe-still for heating heavy oils is highly desirable because the flow of the oil is turbulent, and the time of heating very short. Opportunity for decomposition is therefore very small. The pipe-still has been used in making asphalts, but has not been applied as extensively as it should be in the production of lubricating oil stocks.

Air-cooled Dephlegmators.

Air-cooled dephlegmators are extensively used in the oil industry. Their economy is doubtful both because they are difficult to control with accuracy, and because a cooling surface from 50 to 200 times that required in a water-cooled apparatus is necessary. Furthermore they are open to all of the objections that I have given for water-cooled dephlegmators.

Points to be Considered in Design.

In the foregoing discussion I have been mainly concerned with basic principles and their application, for I feel that it is fundamentals and not mechanical details that have been neglected. I have no intention of discussing matters of design as regards boiler-shop work, foundry work, or fittings. These matters are of great importance, but are familiar to, and capably handled by, engineers in every refinery.

For the student, or the uninitiated, I should mention that in designing equipment for the distillation of petroleum, factors other than those imposed by the requirements of the separation alone must be considered. Water in the oil, salts that hydrolyze with formation of corrosive compounds, other corrosive substances, sediments, tendency to decom-

pose and carbonize, and quantity and quality of the water supply, are among such factors. Each plant will present special problems peculiar to itself that must be thoroughly understood before attempting to lay out the best adapted equipment for distillation.

Column or Tower Packings.

An effective tower packing is one that affords the maximum surface per unit volume filled with the packing, that allows horizontal as well as upward flow and mixing, that allows a free-space of over 90 per cent, that under the particular service conditions is not corroded, and that does not flood or retain excessive quantity of liquid. In some instances, particularly in continuous distillation, it is highly desirable that the packing shall retain moderate quantities of liquid, for this results in slow movement of the liquid down the tower or column.

A packing that is effective for many purposes consists of cylinders whose diameter and length are approximately equal. This is usually referred to as ring packing. A ring packing 1 inch in diameter and 1 inch long, when filled into a space without special placing, offers 60 to 65 sq. ft. of surface per cubic foot of space. The "free-space" is over 90 per cent if the rings are made from a heavy sheet metal. A ring packing ½″ in diameter and ½″ long offers a surface of over 120 sq. ft. per cubic foot, and a large free space. The exact surface and free-space of any packing are easily determined. Packings such as stones, coke, wooden grids, and tiles offer far less surface and free-space than metal rings.

Many sheet-metal packings can be made that are effective. An example is the Foster packing which consists of alternate concentric layers of corrugated and flat sheet metal held together by two steel rods piercing the cartridge transversely and at right angles to each other. The cartridges are made of 28 gauge black or galvanized sheet iron, weigh about 37 pounds per cubic foot, offer about 125 sq. ft. of surface per cubic foot and have a free-space of over 90 per cent. One objection to a packing of this type is the obstruction of sidewise movement of the fluids in the tower or column.

It will frequently be desirable to make tower-packing material out of cast-iron. In order that the walls of such packing shall be very thin it will be desirable to use a high-phosphorus iron and to cast by machine. In this manner the carbon will be kept in cementitic form, and the packing will be resistant to corrosion and abrasion. Such packing will, however, be brittle and must be supported in sections in the tower.

The resistance to gas-flow of a number of tower packings has been studied by Zeisberg[5a] and Taylor of E. I. duPont de Nemours Company. While all of the packings studied by them were quartz, stoneware, or tile, the data given may be useful in a qualitative way to the refinery engineer.

[5a] *Chem. and Met. Eng.*, 21 (1919), 765-6.

TABLE L

CHARACTERISTICS OF VARIOUS TOWER PACKINGS

Packing	X 10^{-7}									Per Cent Free Space	Surface Sq. Ft. per Cu. Ft.	Weight Lb. per Cu. Ft.	No. Units per Cu. Ft.
	f_{dy}	f_{dw}	f_{dc}	f_{sy}	f_{sw}	f_{sc}	f_{py}	f_{pw}	f_{pc}				
Quartz, 6 in.	58	60	60	...	...	...	...	...	...	44	6.3	89	......
Quartz, 3 in.	101	110	139	...	...	...	...	...	...	46	12.7	86	......
Quartz, 2 in.	384	396	433	...	...	...	...	...	...	46	18.7	88	......
Quartz, ½ in. to 1 in.	672	865	1095	...	...	...	...	...	...	47	50.3	88	......
Coke, 3 in.	76	81	94	...	...	...	...	...	...	58	12.7	29	......
Coke, ½ in. to 1⅛ in.	289	380*	....	...	...	...	...	...	...	.....	....	..	......
4 in. x 3 in. smooth diaphragm rings	51	56	63	25	34	38	...	32	34	64(1)	20.0	50	27
										51(2)	27.0	66	36
										51(3)	27.0	66	36
3 in. x 3 in. corrugated diaphragm rings	51	56	63	31	42	58	26	28	28	65(1)	24.0	48	53
										57(2)	30.0	61	67
										55(3)	31.0	63	70
3 in. x 3 in. corrugated spiral rings	45	54	63	54	54	61	...	...	...	72(1)	22.0	40	48
										64(2)	29.0	53	63
6 in. x 6 in. corrugated spiral rings	...	....	....	38	47	50	24	3	35	58(2)	15.0	53	8
										58(3)	15.0	53	8
6 in. corrugated Hechenbleikner blocks	16	36	36	35	38	38	26	...	28	72(1)	10.7	39	4.2
										62(2)	14.3	52	5.6
										62(3)	14.3	52	5.6
1 in. Raschig rings	345	345	345	...	...	...	...	...	...	73	58.0	40	1350
Tile on edge, unstaggered	...	....	....	...	...	...	31	31	43	59	10.5	62	16
Tile on edge, staggered	...	....	....	...	...	...	18	24	31	75	6.4	35	9.5
Tile on edge, staggered	...	....	....	...	...	...	31	33	35	55	11.6	68	17.5
Tile on edge, staggered	...	....	....	...	...	...	43	43	74	45	14.0	81	21
Tile staggered, alternate rows flat	...	....	....	...	...	...	41	48	57	49	13.2	77	20

* Wet with 92 per cent sulphuric acid instead of water.
(1) dumped. (2) stacked. (3) packed.

The gas passed through the towers was air. Pressures at top and bottom of the towers were measured by manometers protected from velocity-pressure effects, and the volume of gas flowing measured by a Pitot tube.

The experimental results are summarized in Table L in such manner as to be used with the following formulation and nomenclature:

Let $s =$ linear velocity in feet per minute.
$p =$ pressure as inches of water.
$k =$ a constant.
$a =$ area of cross-section of the packed-tower.
$h =$ height of the packing in feet.
$v =$ volume of air as cubic feet per minute.

Then, for unit height of packing

$$p = ks^2 \text{ and } s = \frac{v}{a}$$

Hence, for packing of height "h"

$$p = \frac{khv^2}{a^2}$$

This equation may be written

$$p = \frac{fhv^2}{a^2}$$

in which "f" is the frictional coefficient of the packing 1 sq. ft. in area and 1 ft. high. "f" is different for each packing, varies with the manner of disposal of a particular packing in the tower, and varies with the quantity of liquid circulated over the packing.

In order to use "f" as a descriptive symbol it may be written with subscripts as follows:

$f_d =$ packing dumped in the tower.
$f_s =$ packing stacked, that is, arranged in regular layers, but with no attempt to have pieces in one layer in any way related to those in adjacent layers.
$f_p =$ packing packed, i.e., arranged regularly in layers, with axes of pieces in adjacent layers coinciding.
$f_y =$ packing dry.
$f_w =$ packing wet with water, but drained as completely as possible.
$f_c =$ packing with water circulating over it at a rate of 11 lb. per sq. ft. cross sectional area per min.

It is, of course, evident that we may have, for example, $f_{dy} =$ packing dumped and dry, and that quartz or coke can give values only for f_d and not for f_p or f_s.

Frictional coefficients were determined for several packings used under various conditions. These data, shown in Table L, are not

accurate to more than two significant figures, and in some instances the second figure is in doubt.

The data in the table speak for themselves, but a few points may be mentioned. For example it is of interest to note how rapidly the resistance to gas flow increases with decrease in the size of the packing material. This is not entirely a question of surface exposed, as is seen from the fact that as the size of the packing decreases the resistance to flow of gas increases, first less rapidly than the surface, and then much more rapidly.

If the packing is small the resistance to gas-flow is greatly increased by merely wetting the surface. Often the difference in resistance of a dry and a wet packing is greater than the difference between a merely wet packing and the same packing with a much larger quantity of water flowing over it.

The superiority of the manufactured packings over coke or quartz is very evident.

The use of the data in Table L is illustrated by the solution of the following problem taken from Zeisberg's article:

"It is desired to find out what pressure will be necessary to force 250 cu. ft. of air per minute through an absorption system composed of 5 towers 2 ft. in diameter and filled 10 ft. deep with absorption material, when 3-in. quartz is used or when 3-in. spiral rings, stacked, are used, the rate of water circulation being 5 lb. per sq. ft. cross sectional area per minute."

The cross sectional area of the packing is $\frac{\pi 2^2}{4} = 3.14$ sq. ft. The total height is $5 \times 10 = 50$ ft. For quartz f_{dy} would be about $120 \times 10^{-7} = 0.000012$, and for spiral rings about $58 \times 10^{-7} = 0.0000058$ (since the rate of circulation for f_c in Table L was 11 lb. per sq. ft. per min., values are assumed about halfway between f_w and f_c).

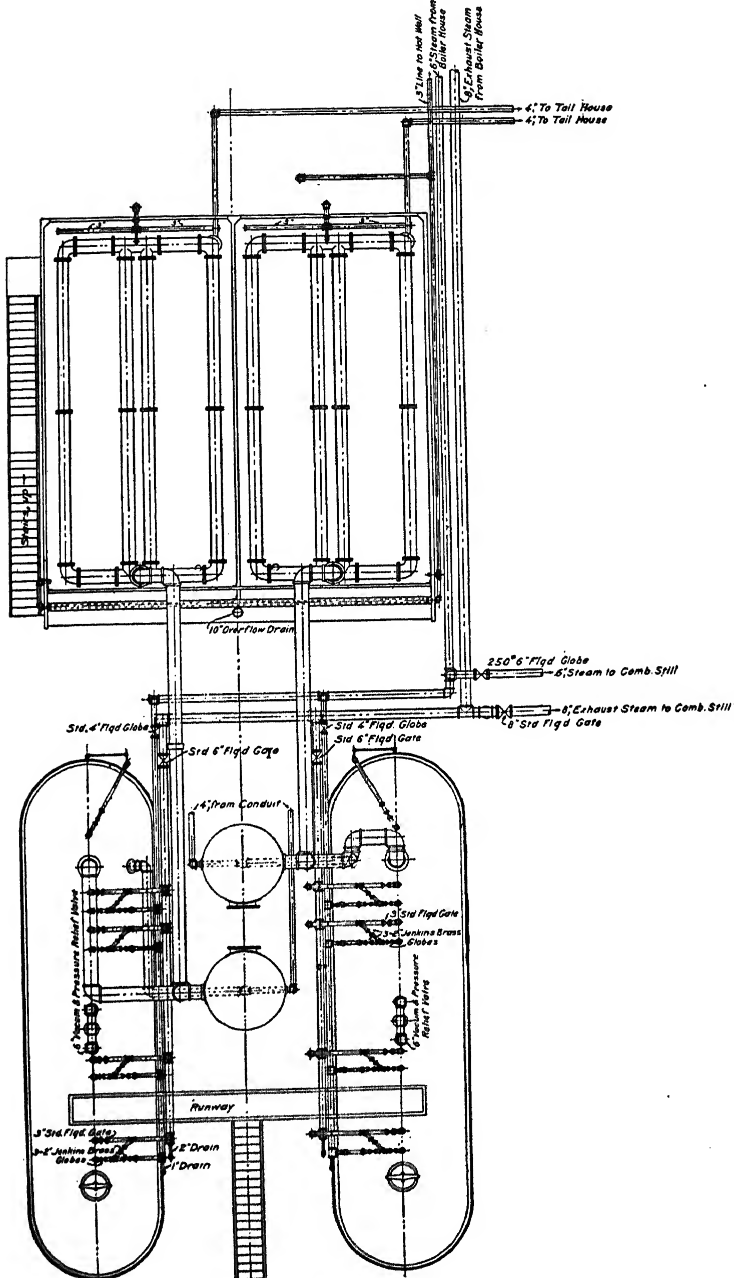
We have seen from equation (5) that the pressure is $p = \frac{fhv^2}{a^2}$, or, substituting numerical values for f, h, v, d,

$$p = \frac{0.000012 \times 50 \times (250)^2}{(3.14)^2} = \frac{0.000012 \times 50 \times 62500}{9.88}$$

$\frac{37.5}{9.88} = 3.8$ in. water for quartz. For spiral rings the pressure would be

$$3.8 \times \frac{0.0000058}{0.000012} = 1.8 \text{ in.}$$

The data of Table L will not be quantitatively applicable to problems in design of towers used in the petroleum industry since there is no necessity for the use of vitreous packings. Nevertheless the information contained in this table will be useful in enabling one to make more intelligent guesses when using packings for which data are not now available. In conclusion, I wish to emphasize that one important



PLAN ABOVE CONDENSER & STILLS

FIG. 78A.—Steam-Stills of the Associated Oil Company at Avon, Calif.

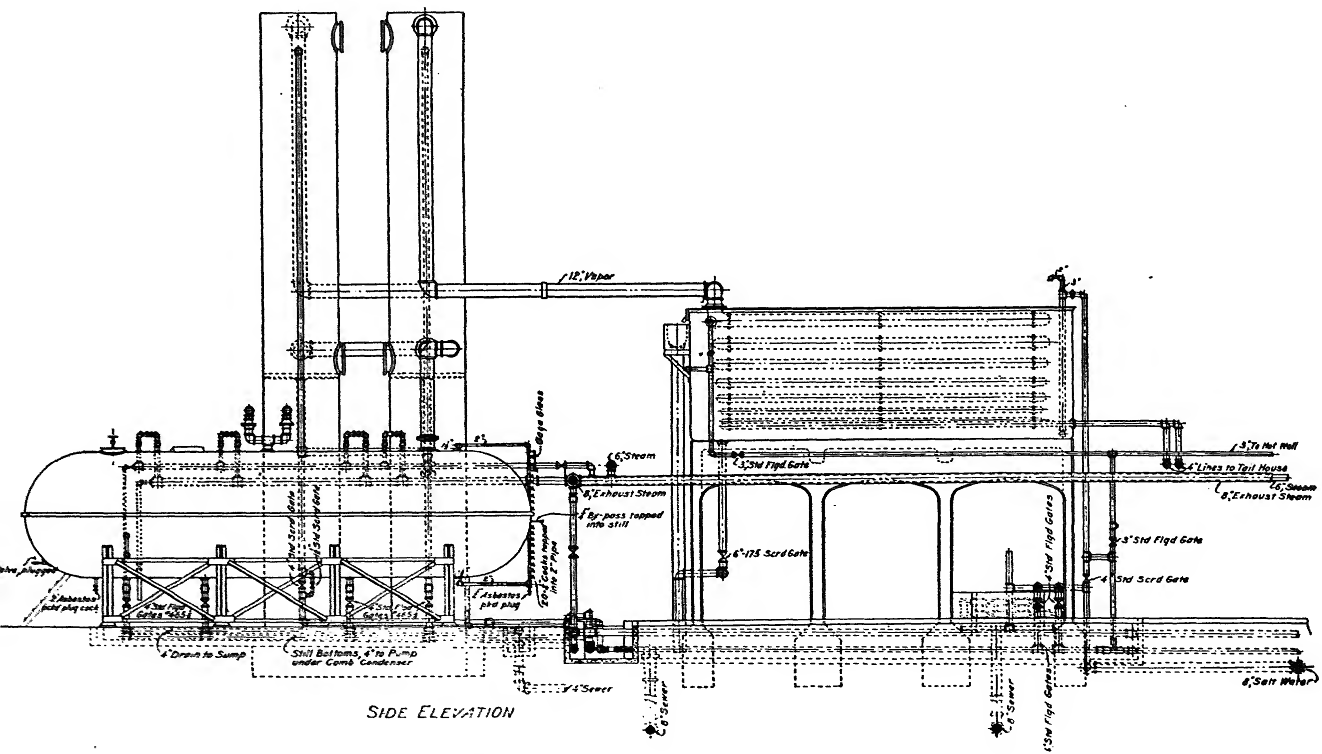


FIG. 78B.—Steam-Stills of the Associated Oil Company at Avon, Calif.

advantage of the packed tower over bubbler-cap columns is the low resistance to the flow of gas or vapor.

Steam-Distillation Methods and Equipment.

Steam-distillation is at present used in refinery practice for re-running gasoline, for reducing burning oils to flash, and lubricating stocks to desired viscosity. I am concerned here only with methods for handling the lighter distillates, although much of the discussion is applicable to the distillation of the heavier oils. The theory of steam-distillation has been briefly reviewed in Chapter IV. It will be recalled that the use of steam allows distillation at lower temperatures than would otherwise be possible, thus preventing decomposition. Also, steam has a sweetening effect that may be the result of hydrolysis of compounds contained in the distillate, together with the solvent action of water for mal-odorous compounds or hydrolytic products. The thermal decomposition of volatil hydrocarbons as a result of distillation without steam is absolutely negligible. If a light distillate is of worse odor after fire distillation, it is the result of decomposition of sulfur, nitrogen, or oxygen compounds contained in the distillate. These may have been contained in the raw distillate, or they may have been introduced through refining with sulfuric acid or other reagents. Whatever the source of these compounds, their decomposition depends on two factors: first, the temperature to which the distillate is heated, and second, the time the distillate is heated. The lower the temperature, and the less the time of heating, the better.

If the raw distillate does not contain bad-odored or corrosive substances, steam-distillation is not only unnecessary but highly uneconomical. The more extensive use of cracking processes has resulted in the production of a large quantity of light distillate that is of necessity refined with sulfuric acid. The refined distillates must be re-distilled in order to render them water-white, and to remove high-boiling olefin polymers. This distillation must be so conducted as to avoid decomposition of compounds in the oil as well as excessive polymerization of olefin components.

In general, steam-distillation should be used only when absolutely necessary, for it requires the combustion of from four to six times as much fuel, if steam is used both for heating the oil and obtaining the tial pressure effect, as when the fuel is used to heat the oil directly, to distill it at its normal boiling temperature. Some plants have quantities of exhaust steam from pumps and engines. This can nomically used in steam-distillation, but even then, unless an is available, steam should not be used for heating but simply aining the partial-pressure effect. If the partial-pressure effect is necessary, the steam may be superheated by placing steam- coils in the last pass of the pipe-still furnace or other com- chamber, provided the maximum partial-pressure effect, obtain- ly with wet or saturated steam, is not required.

Several types of apparatus are used for steam-distillation in current refinery practice. The stills shown in Figure 78 from Bulletin 162, U. S. Bureau of Mines, are those of the Associated Oil Company at Avon, California. These stills are 10 ft. in diameter and 40 ft. long, and contain four compartments. Steam is admitted from six perforated 2-in. pipes in each compartment, and steam for heating circulates through 45 lengths of piping in each compartment. The tower is 6 ft. in diameter and 50 ft. high, and filled with tile. The details of this equipment have been given by Wadsworth[6]—and need not be repeated here.

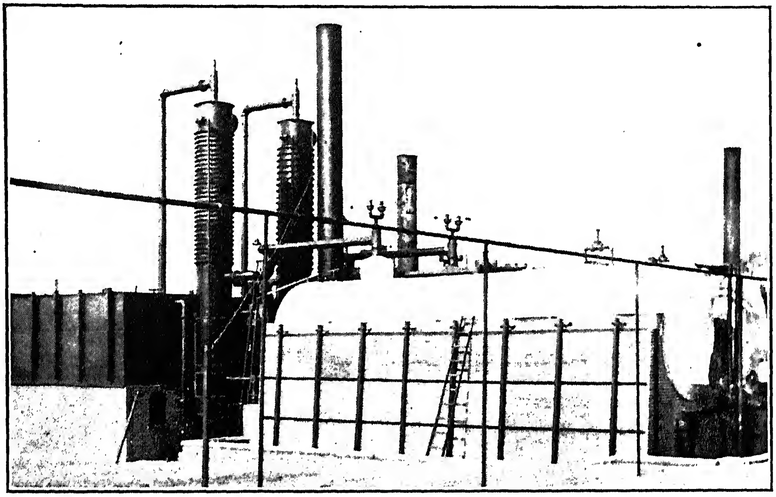


FIG. 79.—Fire and Steam Re-Run Stills of the Texas Oil Products Company at Waxahachie, Texas.

The combination fire- and steam-stills used by the Texas Oil Products Company are shown in Figure 79.

I have personally never been able to make my views on steam-distillation coincide with current practice as I have observed it. For example, I fail to see the necessity of a large still such as that shown in Figure 78. Steam-distillation differs not at all from distillation without steam except in regard to the partial pressure relationships. Each is a process of continuous change in the composition of vapor and liquid, and accordingly each should be conducted in an apparatus that provides for the necessary intimate contact of liquid and vapor. The still with the large body of liquid through which steam is blown cannot do more in the way of separation than is accomplished by one perfect column section. Hence, why spend money for a large still when one-tenth the

[6] *Bull. 162,* U. S. Bur. of Min.

sum spent in column construction will do the same work. Furthermore, if sweetening is desired, it is necessary to have intimate contact of both vapor and liquid hydrocarbons with liquid water. This is easily obtained in a good column apparatus. Hence, if it is a question of separating a small quantity of heavy distillate from a large quantity of lighter distillate as in re-running gasoline, I consider an apparatus[7] constructed along the same general lines as that shown diagrammatically in Figure 77 the most effective and efficient for steam-distillation. The use of heat exchangers, preheater and prevaporizer is desirable. The pipe-still heater avoids the excessive cost of heating by steam, and eliminates decomposition because the time of heating is so short. Steam is introduced beneath the packing in the vaporizer in quantity sufficient to produce the desired result. Provision must be made to drain all of the water from each section, for otherwise it would accumulate to the exclusion of the distillate that it is desired to draw off. If only gasoline and bottoms are to be made, the taps for liquid on each section can be omitted, and the packing supported on perforated shelves. In this case, also, only such portion of the condensate would be returned to the top of the column as was found necessary to give the separation required.

If a small amount of volatil distillate is to be removed from a large quantity of less volatil oil, as in the reduction of kerosene to flash, the vapor from the vaporizer should be introduced into a section part way up the fractionator. The lower sections will then function as an exhausting column. The steam should be introduced into the lowest section of the fractionator. The taps for liquid in the lower sections would not be needed.

Condensers for Steam-Stills.

A common error is to provide too little surface for condensation in steam-distillation. This mistake is made because the total heat of one pound of steam is eight to ten times the total heat of a pound of gasoline vapor. Condenser surfaces should be based on the total number of B.t.u. to be transferred.

Condensers, Heat-Exchangers, Coolers.

I have intimated in Chapter V that present knowledge of heat-transfer phenomena is so fragmentary that it affords no basis for exact design. To be dogmatic in discussing apparatus for transferring heat is either to admit a willingness to err, or is a confession of ignorance of the true state of knowledge in this field. A few principles may be ...ed as fairly well established but can be used only in a qualitative ... tly seen apparatus in use that vio- ...ls, and therefore, at the risk of

... covering a process and apparatus of ... been filed.

repetition, I shall briefly review these principles and discuss a few apparatus with them in mind.

The fact that the greatest resistance to the flow of heat from one fluid through a metal wall to another fluid lies in the slow moving or stagnant fluid films on each side of the metal wall must be appreciated if apparatus for transferring heat is to be properly designed. As I have already stated in Chapter V, the resistance of a gas-film is much greater than that of a liquid-film. For this reason, an effort should be made so to design apparatus that conditions will be as favorable as possible for heat-transfer on the gas-side even though this may involve a sacrifice of best conditions on the liquid-side. However, liquids frequently contain dissolved gases that are evolved as the liquid is warmed, or contain substances that vaporize when the liquid is heated. In either of these cases, the resistance to the transfer of heat on the liquid-side of the heating surface will be comparable to that on the gas-side.

The recognised method of reducing the film resistances to heat transfer is to increase the velocity, or more properly the mass-velocity, of the fluids. In all cases, the velocity of the fluid should be greater than the greatest critical velocity, for if the average velocity is less than the critical, the velocity at the surfaces of the metal wall separating the fluids is zero. When the fluids move at rates greater than the critical velocity, the flow is turbulent, and the thickness of the stagnant or slow-moving fluid film next the metal wall is reduced, with a consequent increase in the rate of heat-transfer. The greater the velocity the better in so far as rate of heat-transfer is concerned. The relationship between mass-velocity and rate of heat-transfer is not linear, for, as was seen in Chapter V, the quantity $\left(\frac{W}{A}\right)$ was introduced into equations with an exponent of 0.75 to 0.80. Economy of operation limits the velocity, because as velocity increases, the pressure required to force the fluid through the apparatus also increases. A compromise must be made that will take into account costs of apparatus for transferring heat, operating costs, and depreciation.

A further factor that enters into the design of equipment for transferring heat is the mean distance of all particles of the fluid from the heat transferring surface. This is taken into account in mathematical expressions by introducing a term called the shape-factor, or less broadly, the hydraulic-radius. Qualitatively, it is clear that the less the mean distance between the particles and the surface, the more rapid the transfer of heat. The convective factor in heat-transfer, of which I have spoken in Chapter V, is affected by the mean distance just mentioned. Although the convective factor is of much less importance than the film resistances, it cannot be entirely neglected.

Other theoretical considerations of less importance may enter into a discussion of heat-transfer phenomena, but those already mentioned are the most important. In addition, many practical points must always be taken into account in design. Simplicity and the use of standard parts are always desirable from the standpoints of initial cost and easy

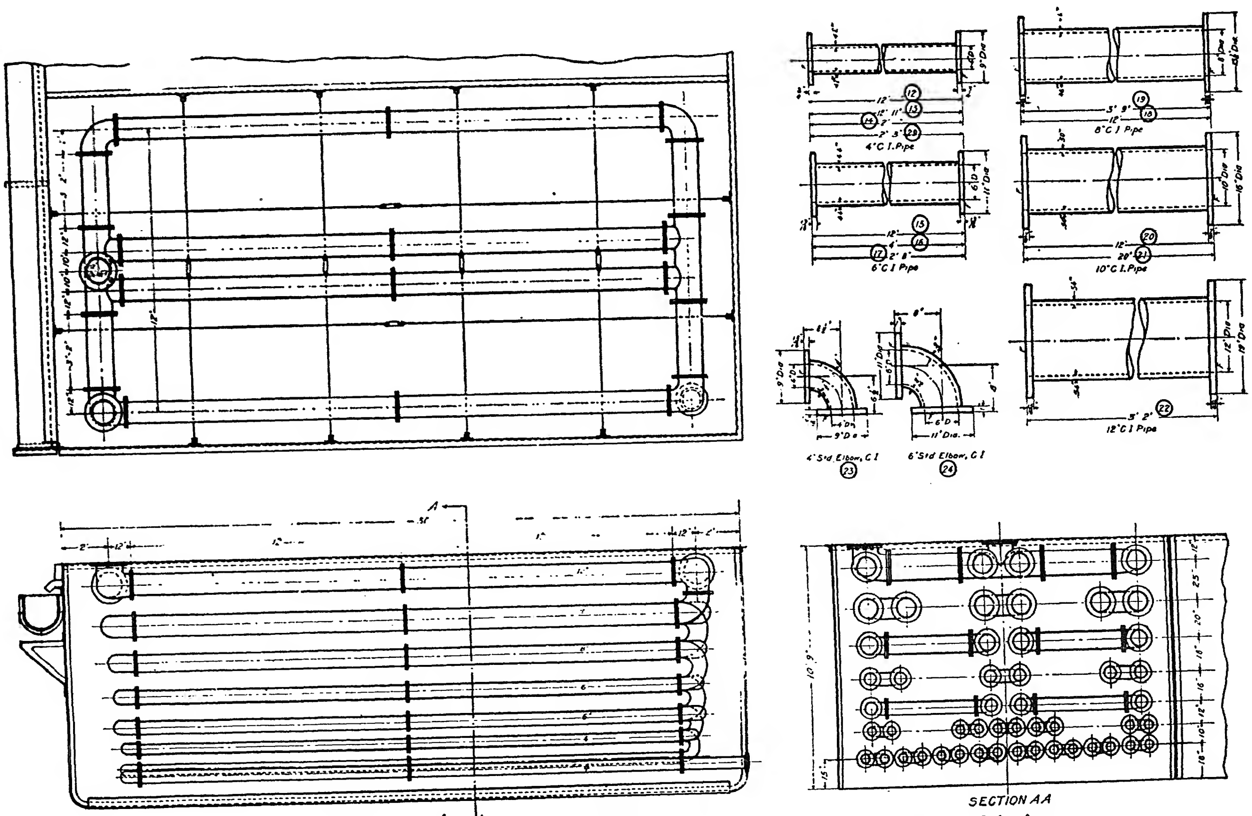


FIG. 80.—Box-Condenser. Design Based on Nearly Constant Vapor Velocity.

replacement. Apparatus should always be so made that it can be easily cleaned. Suitable engineering materials must be selected. These and many other practical points will demand thought in each instance.

With the foregoing considerations in mind, I wish briefly to discuss the merits of a few apparatus.

Condensers.

The condenser is one of the most important apparatus used in an oil refinery. Too often it is designed largely on the basis of precedent. Only in the last few years has condensing equipment begun to show the earmarks of application of physical and engineering principles. It is pleasing to observe that real progress is now being made.

In the following paragraphs, I shall describe pipe-coil condensers, tubular condensers, and several special condensers.

The Box-Condenser.

The oldest, and still a common type of condenser used in the petroleum industry, is the "box-condenser" with its submerged pipe-coil. The inefficiency of this condenser as ordinarily designed is slowly being recognized, and the use of other types is increasing.

The usual submerged condenser-coil consists of several lengths of 10-in. or 12-in. steel or cast-iron pipe followed by lengths of 8-in., 6-in., and 4-in. pipe, each length 30 to 40 ft. long, and all connected into a continuous coil several hundred feet long by means of return bends. A condenser of this type is shown in Figure 80. Cast-iron pipe, although heavy and awkward, is used in all cases when sea-water is used for cooling or when corrosion is thought to be likely on account of action of acidic gases resulting from the hydrolysis of salts in the water emulsified in the crude, of the presence of corrosive sulfur compounds, or for any other reason.

Design of coils for box-condensers has of necessity been empirical. An allowance of 1.5 to 2 sq. ft. of condensing surface per gallon of gasoline or naphtha per hour, of 1.2 sq. ft. for kerosene, and 1.0 sq. ft. for heavy oils, is usual, but empirical figures must be modified to fit the particular conditions. The data just given are equivalent to designing on the basis of

$$H = 13.5 \text{ to } 18.5 \text{ B.t.u. per hour per sq. ft. per } 1^\circ \text{ F.}$$

A. D. Smith[8] uses $H = 25$ when designing a cast-iron condenser coil when the supply of cold water is ample. This in the particular case discussed by him is equivalent to using 1.25 sq. ft. of surface per gallon of condensate per hour. If the water supply is limited he suggests the use of $H = 50$. An extensive tabulation of data, compiled by the American Radiator Company, and useful in the design of condensers for various distillates is reproduced by Smith.

[8] "Handbook of the Petroleum Industry."

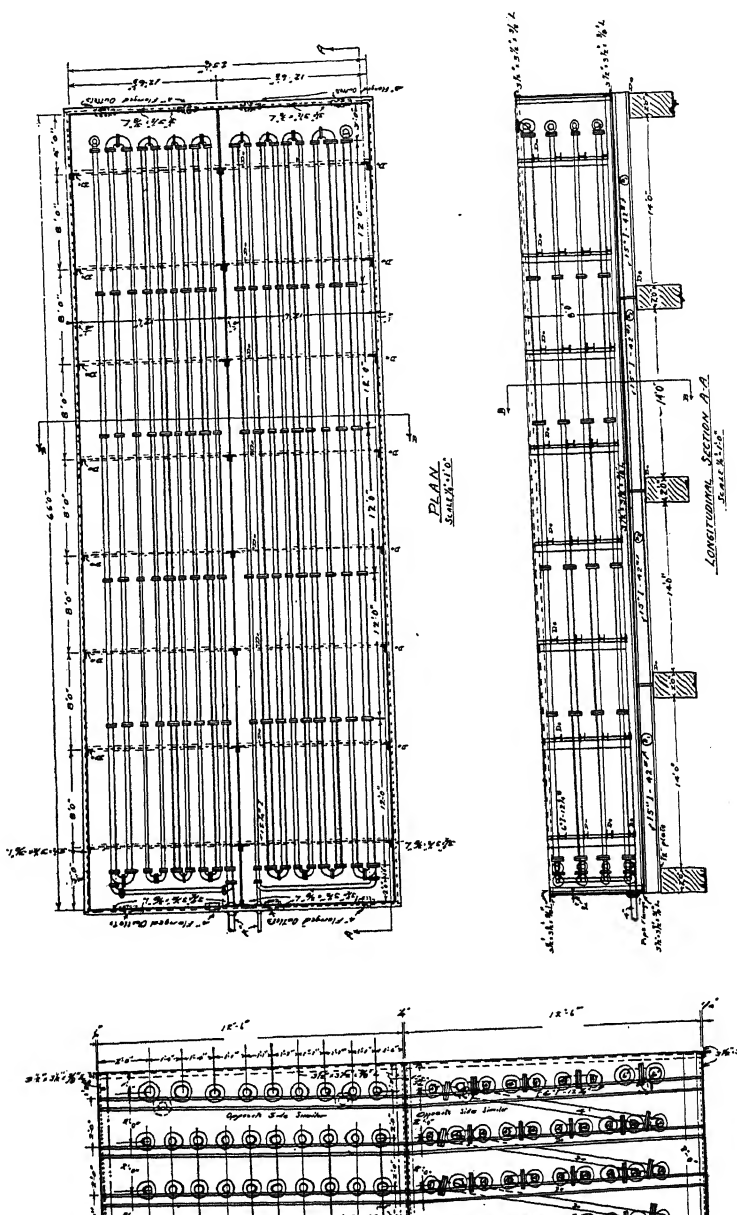


Fig. 81.—Box-Condenser Used by Greenstreet.

The customary practice of decreasing the size of the pipe from the inlet to the outlet end of the coil was probably originally based on the simple idea that a large pipe was necessary to handle a large volume of vapor, but that smaller pipe could be used as the volume of vapor became less. The assumption is that vapor velocity should be roughly constant. The guiding principle should be to make vapor velocity as great as is possible without undue pressure in the still. The relationships between pressure and velocity, as given in the first part of Chapter V, should be used to determine a suitable pipe-size. Obviously, the rate of heat-transfer, or the value of H, depends on pipe-size, for this determines velocity and also the shape-factor.

Redwood [9] cites the use of an allowance of 0.05 sq. in. of cross-sectional area of pipe per gallon of gasoline per hour in calculating the diameter of the first pipe in a condenser. This is equivalent to basing design on a vapor velocity of 10 to 15 ft. per second. Appropriate decrease in pipe size should be made if velocity is to be maintained constant.

On the other hand, pipe size may be the same or nearly the same throughout the length of the coil and velocity and pressure may be allowed to vary. A condenser designed on this basis and used by Dr. Greenstreet is shown in Figure 81. This figure also illustrates the general construction of the condenser-box. The manner of connecting the pipes of the coil, the supports for the coil, the pitch of the coil, the angle-stiffening of the 1/4-in. tank-plate used to make the condenser-box, the water inlets and outlets, and the beams for supporting the box are shown.

The condenser with submerged coil is possessed of several inherent faults. The most important of these is that the velocity of the cooling water is very low. This results in an extremely low rate of heat-transfer, partly because the water moves slowly, and partly because the dissolved air that separates and adheres to the pipe-surfaces is not swept away. Further than this the condensate runs along the bottom of the pipe and thus is not brought into intimate contact with the vapor and gas. The result of this lack of scrubbing is that the tail-gases contain valuable volatil hydrocarbons that should have dissolved in the condensate.

The box-condenser because of the low rate of heat-transfer is always a large awkward apparatus. Because of its size and weight it costs more than the smaller efficient condensers. Unless the condenser is designed in such manner as to allow easy access to all parts, and I have seen few that were so designed, the removal of the calcium carbonate and sulfate scale is a difficult job.

One important advantage possessed by the box-condenser is the fact that it contains a large volume of water. The stoppage of a pump is thus not a serious matter as it is with other condensers that depend on rapid water-circulation and contain only a small quantity of water at any time.

[9] "Treatise on Petroleum."

The Vento condenser sections of the American Radiator Company have been pictured in Figures 67 and 68 of Chapter VI.

Coil-Condensers Cooled by Sprays or by Trickling Water.

In hot dry climates the box-condenser with submerged coil is an unsatisfactory apparatus. The water is cooled by circulation over cooling towers or in spray ponds, and, although the cooling effect of vaporization of a part of the water may be entirely satisfactory, the water in ponds or reservoirs is warmed again by absorption of the sun's radiation.

Properly cooled water for use in submerged coils is thus difficult to obtain. This led to the use of pipe-coils mounted within louver towers in such a manner that the cooled water from the tower was collected

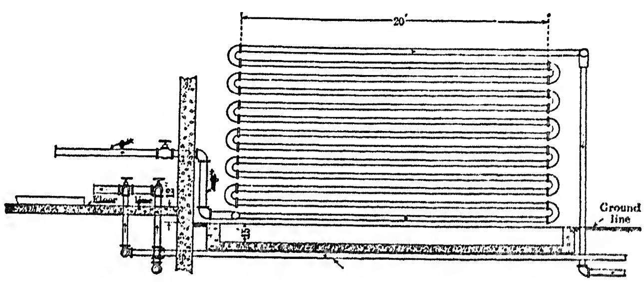


FIG. 82.—Pipe-Coil Condenser. Water Trickling Over Surface of Coil.

and trickled over the coils placed below the cooling-tower proper. Since in hot dry climates it is possible by partial vaporization to cool water 10° F. to 35° F. below the temperature of the air, satisfactory results are obtained with apparatus of this type.

The advantages of this type of condenser or cooler are not fully appreciated, and its utility is not restricted in any way to hot dry climates. The pipe-coil over which water trickles is a distinct improvement over the submerged coil in that the velocity of the cooling water is sufficient greatly to increase the rate of heat-transfer. This type of condenser has been widely used in the natural-gas gasoline industry and a citation from pp. 67-68, Bulletin 176 of the U. S. Bureau of Mines ill serve to illustrate my point. In condensing the vapor from the that separates gasoline from the absorption oil some plants use ged coils and others coils in louver towers. The typical sub- coil is designed on a basis of 3.5 to 4.0 sq. ft. of surface per gallon of gasoline per hour, whereas 2.5 sq. ft. is the usual figure for design of coils in louver towers. These figures are both higher than would be used if the coil were to produce condensation of a vapor alone. In addition to condensation of gasoline they must cool gases and vapors that do not condense, but whose presence greatly decreases the rate of heat-transfer.

The louver-tower coils are usually made by connecting lengths of 2-in. pipe with return bends as shown in Figure 82. When used in parts of the country where the climate is not hot and dry they need not be placed in a cooling tower, but may be arranged so that cold water

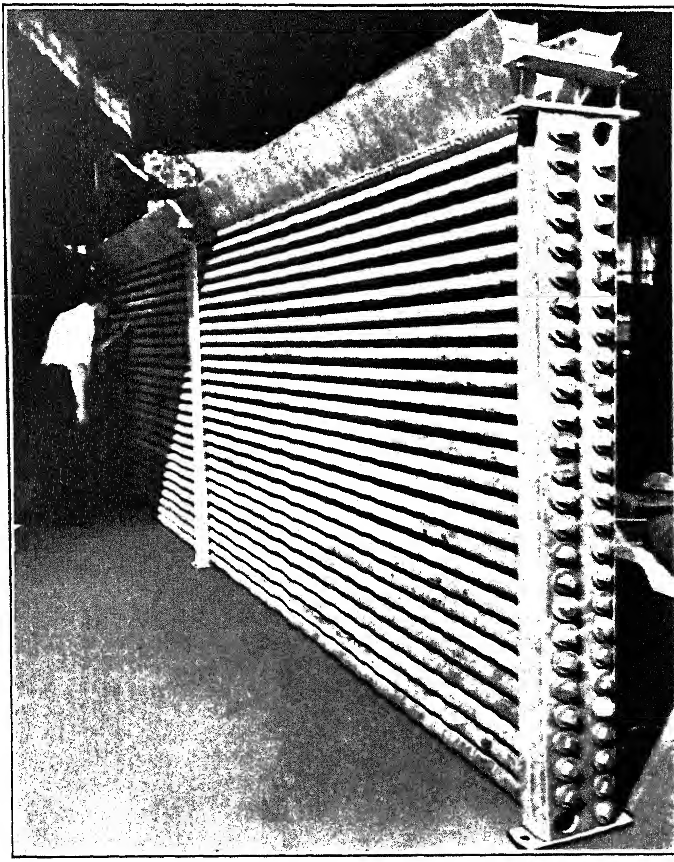


FIG. 83.—Steere Tube-Stack.

is pumped to them and distributed so that it flows downward over the surfaces. A well designed pipe-stack is made by the Steere Engineering Company of Detroit. This is shown in Figures 83 and 84. The surface of the pipes, inside and out, is readily accessible. Tubes can be replaced without disturbing the others in the stack. The standard stack is 26 tubes high, 20 feet long and made of 2-in. boiler tubes

expanded into ½-in. steel headers. Division plates are welded into the headers in such a manner that all tubes are connected in series. The volume in each return-bend space is 50 per cent greater than in a standard pipe return-bend. Frictional resistance is thus reduced. The space between tubes is only ¾ in., which makes wind-strips unnecessary and yet permits of free air circulation. The entire apparatus is heavily coated with zinc after fabrication, and they are being used successfully with sea-water as a cooling liquid.

Pipe-coils such as are here described can be used both as condensers

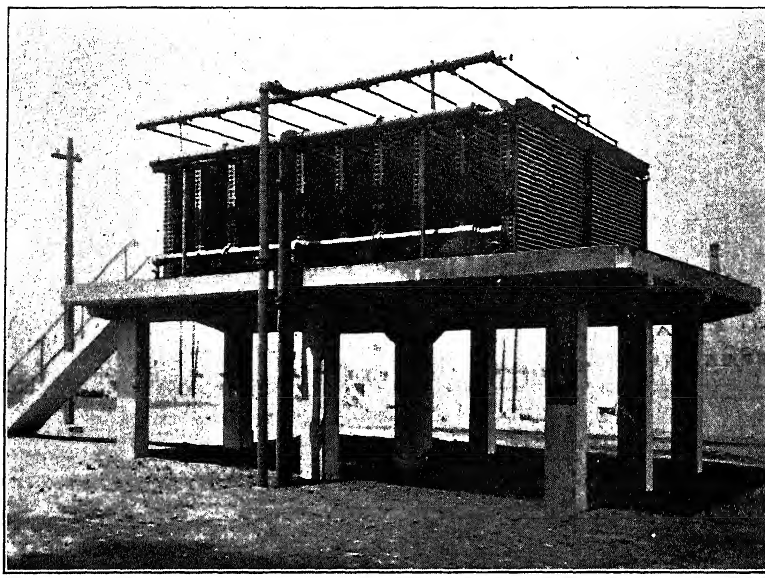


FIG. 84.—An Assembly of Steere Tube-Stacks.

and coolers. When used as a condenser the condensate will be run through a cooler. This is necessary because the water in the lower coils of the condenser is warm as a result of its contact with the coils above, and the distillate does not leave the condenser as cold as it should.

The flow of vapor in a pipe-coil condenser should be downward, that is, vapor and liquid should travel in the same direction. If they travel in opposite directions the downward flow of the liquid is impeded by the gas with the result that the rate of heat-transfer is lowered on account of the thick film of liquid in the pipe. It would be desirable in some ways if the vapor could be introduced into the bottom of the coil, for then the flow of vapor and of cooling liquid would be counter-

current, and, more important still, non-condensible gases would be swept along more effectively than when the vapor flow is downward. An apparatus can be so made that the liquid condensate is trapped from each pipe, in which event the objection to countercurrent flow of vapor and liquid is largely nullified. However, this introduces complications from a mechanical standpoint that are hardly justified.

Sterling Condensing Sections.

The Sterling condensing section shown in Figure 85 is made by the American Radiator Company. The claim is made that in comparative tests the Sterling section shows a condensing capacity 20 per cent greater than a pipe of comparable dimensions. The sections are made

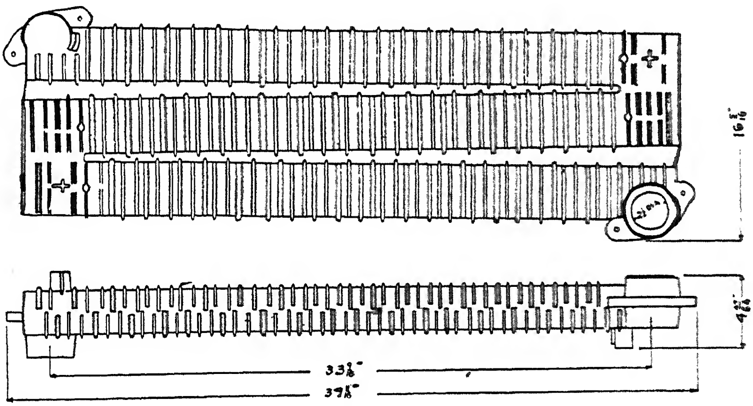


Fig. 85.—Sterling Condensing Section.

of cast-iron of ⅜-in. thickness, weigh 137 pounds each, offer 14 sq. ft. of surface, are fitted with 2½-in. flanged openings, and are of 39¹¹⁄₁₆ x 16⁵⁄₁₆ x 4¾ in. over-all dimensions. They are tested to 100 pounds hydrostatic pressure, but are to be used for low pressure work only. The section is so compact that a condenser box only one-half the size of that required for an ordinary submerged pipe-coil is necessary for the same condensing surface. This is true even though the Sterling sections are arranged far enough apart to allow easy access for cleaning all exterior surface. Repairs are also very easily made.

The Sterling section may also be cooled by trickling water downward in a manner similar to that already described for pipe-coils. This, in fact, is the most desirable way in which to use them. The first equipment of this nature is shown in Figure 86. This was layed out by Dr. C. M. Alexander, Manager of the Texas Oil Products Company.

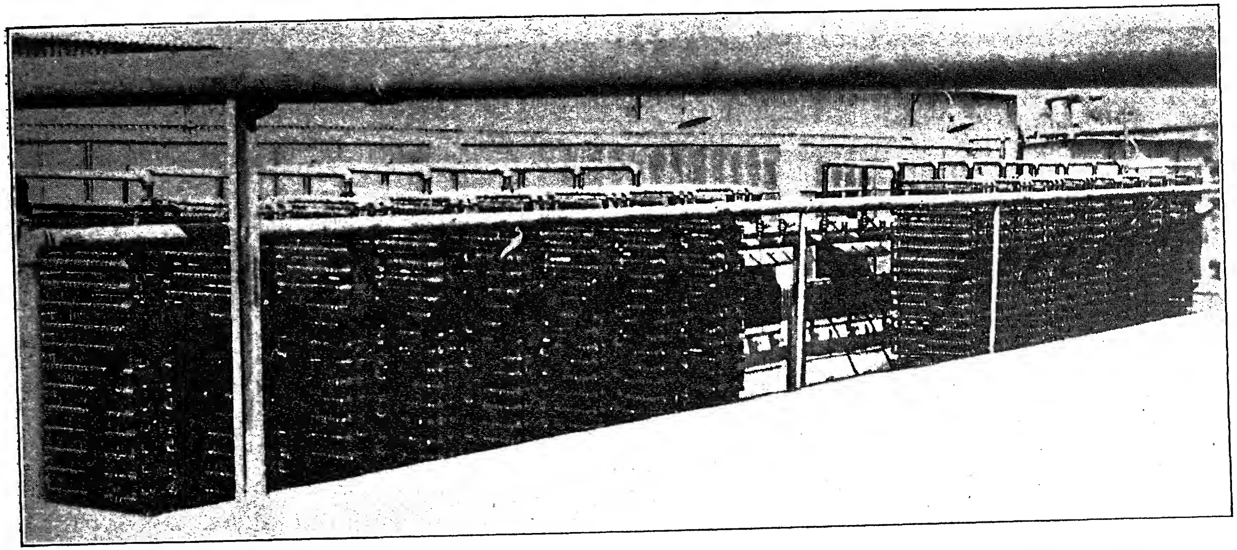


FIG. 86.—Sterling Condensing Sections as Used by the Texas Oil Products Company, Waxahachie, Texas.

Tubular Condensers.

The tubular condenser is a product of adaptation of steam engineering practice to refinery engineering. This type of condenser has been extensively used in topping and skimming plants. Transfer of heat in Trumble plants is accomplished almost exclusively by the use of tubular apparatus. The main advantage of this type of condenser is its compactness. Another good feature that is not always recognized is the fairly intimate contact of vapor and condensate. The scrubbing is sufficient so that light hydrocarbons, condensed ineffectively by cooling alone, are dissolved in the condensate. The loss of valuable hydrocarbons in the tail-gases from properly designed and operated tubular condensers is small.

The main disadvantage of the tubular condenser is the low rate of heat transfer resulting from the relatively low velocities of both water and vapor. Effort is usually made to increase the rate of heat transfer

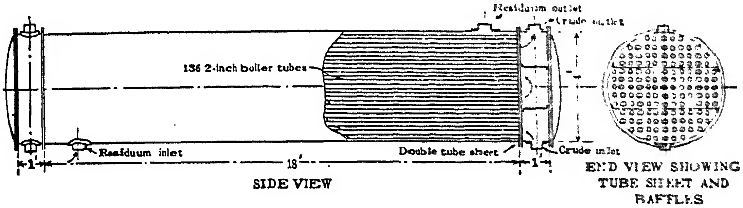


FIG. 87.—Tubular Condenser Used by the General Petroleum Corporation.

by the use of baffles. This is illustrated in Figure 87, that shows a 48-in. condenser used in the Trumble plant at Vernon, California. This apparatus contains 136 2-in. boiler-tubes. The outside tube-surface is 1,280 sq. ft. and the inside 1,158 sq. ft. The newer 48-in. condensers used at Vernon contain 258 2-in. tubes 18 ft. long. The flange sheet is layed out with a 5/8-in. 60° bridging. That is, the centers of the tubes are 2 5/8 in. apart along one line, and also along another line at an angle of 60° to the first. The external cooling surface of the tubes in this condenser is slightly over 2300 sq. ft. The value of H for these condensers is 6 to 8 B.t.u. per hour per sq. ft. per 1° F.

A mechanical improvement in these condensers would consist in making a tube-basket that could be lifted out of the shell for cleaning or for repair. Also the baffling should be such that the cooling medium would be forced to follow a longer path and thus move more rapidly. This has been done in the multiwhirl condensers and coolers described below.

A further disadvantage of the tubular condenser lies in the necessity of skilled labor for making repairs. The entire apparatus is somewhat intricate, and while a boiler-shop will always be a part of the organiza-

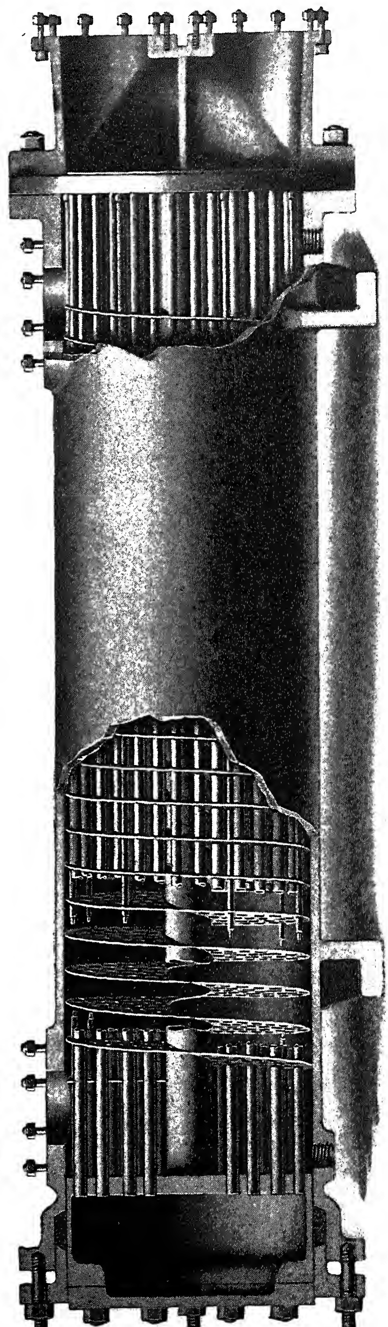


FIG. 88.—Griscom-Russell Multi-Whirl Condenser.

tion of a large refinery, the smaller operator may be embarrassed by lack of facilities and skilled help.

The Multiwhirl Condenser.

The multiwhirl condenser made by the Griscom-Russell Company and shown in Figure 88 is a well designed tubular condenser. The vapor enters the ⅝-in. tubes at the top. The water enters the space around the tubes at the bottom and travels upwards in the space between the helical baffles. This condenser is very compact, brings the condensate into fairly intimate contact with the non-condensible gas, and as a result of increased velocity of both vapor and cooling water brings about a much more rapid transfer of heat than the ordinary tubular apparatus. The floating head construction eliminates strains on the tube joints. The tube bundle can be readily removed for inspection and cleaning.

The Southwestern Condenser.

A compact and efficient tubular condenser is made by the Southwestern Condenser Company. This apparatus is shown in Figure 89. It is built in sections, each of which contains three tube-banks or units. The body-casting is made of semi-steel. The ¾-in. tubes are made from admiralty metal exclusively, since experience as well as experimentation with steel, brass, copper, monel, admiralty, tinned, and nickeled tubes showed the admiralty metal tubes to be most satisfactory. Each section is equipped with six cover-plates, any one or more of which is easily removed when the tubes are to be inspected or cleaned.

The condenser shown in Figure 89 is 8 ft. 10 in. high, and the cross-section of the body-casting is 30 in. by 30 in. Each of the nine banks of tubes offers 60 sq. ft. of condensing surface, and the entire condenser 540 sq. ft. Vapor enters the top of the apparatus, and passes downward around the tubes. Obviously, ample opportunity is afforded for contact of condensate and vapor. Because of the thorough scrubbing, the tail-gas from this condenser will contain little else than non-condensible gases. The water enters the bottom tube-bank, and flows through the tubes. Baffles are so cast on the cover plates that the water makes three or five passes in each tube-bank. Three-way valves are so arranged that any tube-bank can be by-passed. This allows inspection or cleaning of the tubes without disturbing the operation of the condenser as a whole. The three-way valves also allow use of the tube-banks either in series or parallel. Furthermore, the bottom sections can be cooled with water while the upper section, functioning as an heat-exchanger, is cooled with oil.

The type B-540 apparatus shown in Figure 89 is guaranteed to condense 25 to 27 barrels of 60° Bé. gasoline per hour and to cool the gasoline to within 3 to 5° F. of the temperature of the inlet water. This allows a 20° F. rise in the temperature of the cooling water. The

guaranteed condensation rate is equivalent to use of H = 27 to 30 B.t.u. per hour per sq. ft. per 1° F. as a safe factor in design.

The apparatus shown in Figure 89 can also be used as a heat

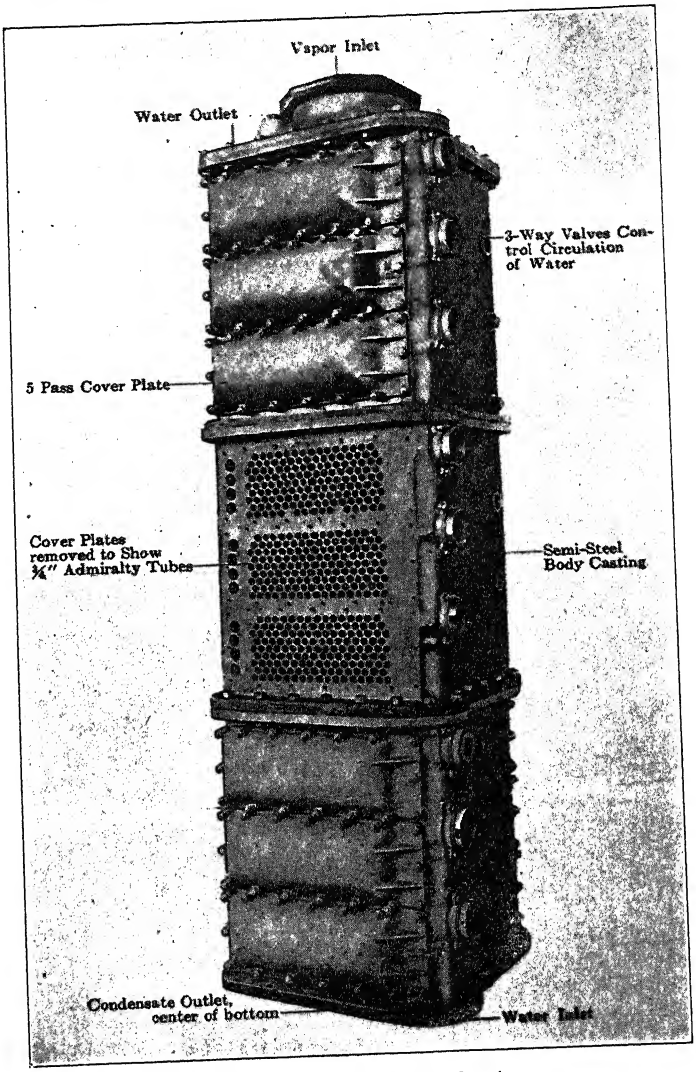


FIG. 89.—The Southwestern Condenser.

exchanger or cooler. When used as an oil to oil heat exchanger, the value of H has been found in practice to be 25 to 35 B.t.u. per hour per sq. ft. per 1° F.

Double Pipe-Coil Condensers.

The double pipe-coil can be used as a condenser, but is more frequently used as a cooler or heat-exchanger and is therefore described below in the latter connections.

Value of the Over-All Coefficient of Heat Transfer in Condensers.

Values of H, the over-all coefficient of heat transfer, for condensers of several types have been given in the foregoing paragraphs. It is of interest to compare these with those used in designing apparatus for the condensation of steam. The latter vary from 100 to 1000 B.t.u. per hour per sq. ft. per 1° F. depending on the steam and water velocities. Values of H between 200 and 300 are used in the design of condensers for steam. Steam velocities are usually between 7 and 10 feet per second although the actual velocity is determined with difficulty.

As has already been noted in Chapter V, McAdams and Frost found the value of the film coefficient "h" in the condensation of carbon tetrachloride and for benzene to be 280 and 340 respectively as compared to an "h" of 2400 for steam. If the values of "h" are divided by the thermal conductivities and fluidities of the respective liquids the eightfold difference between the values of "h" for steam and for the organic liquids becomes only a twofold one. The low coefficients in the case of organic liquids such as the hydrocarbons are thus seen to be the result, in part at least, of differences between properties of these substances and water, and not entirely the result of unintelligent or careless design.

Emergency Water Supply.

When any apparatus that does not contain a large volume of cooling water is used as a condenser, provision should be made for an emergency water supply. Connection to a standpipe or other source of water, and means for automatically admitting this water to the condenser in the event of accidental stoppage of the regular supply of water, will eliminate possible loss and danger.

Air as a Cooling Medium.

Air is occasionally used as a cooling medium, though this is usually limited to the cooling of dephlegmators or partial condensers. In general this practice is undesirable, for on account of the very low thermal conductivity of nitrogen and oxygen the cooling surface required will be 50 to 200 times that necessary if water is used. Even under favorable circumstances the value of the gas-film coefficient "h" will be only about 2 B.t.u. per hour per square foot per 1° F. Large, costly, and

unwieldy apparatus is therefore required. Furthermore air cooling is controlled with difficulty, and often for this reason, if for no other, should not be considered.

Coolers.

The same types of apparatus that have been described as condensers, and will be described as heat-exchangers, are also used as coolers. The rates of heat transfer will not be the same, however, as these depend on conditions in the particular case.

A submerged pipe-coil consisting of 960 ft. of 4-in. pipe placed in a 6 ft. x 8 ft. x 20 ft. tank is used as a cooler at the Tecomate plant of the Atlantic Gulf Oil Co. In a particular instance the hot topped crude oil entered at a temperature of 377° F. and left at 325° F. The water entered at a temperature of 78° F. and left at 100° F. 425 barrels or 138,550 pounds of oil were cooled per hour. The total surface of the coil is 1000 sq. ft. The value of Θ_m was 263° F., and the value of $H = 12.3$ B.t.u. per hour per sq. ft. per 1° F.

Data covering the operation of a pipe-stack cooler of the type shown in Figure 82 are given by Dykema.[10] The coil contained 13 20-foot lengths of 4-inch pipe. An allowance of 4.0 sq. ft. per gallon of absorption-oil per minute was made in designing this coil. The oil is cooled from 150 to 80° F. Complete data are not given, but by making reasonable assumptions it appears that the value of H is about 57 B.t.u. per hour per sq. ft. of external surface per 1° F. The velocity of the oil is 1.8 to 1.9 feet per second. If 2-in. pipe is used in coils of this nature an allowance of about 3.0 sq. ft. per gallon of absorption-oil per minute is made.

H. H. Cooper[11] states that an allowance of 15 to 20 sq. ft. of cooling surface should be made per 1000 gallons of absorption-oil circulated per 24 hours. This is equivalent to 21.6 to 28.8 sq. ft. per gallon of oil circulated per minute, or between 7 and 10 times the area cited by Dykema. The velocity of the oil in the cooler should not be over 120 ft. per minute or 2 ft. per second, for otherwise friction losses are excessive.

The discrepancy between Dykema's and Cooper's design data demands some comment. Cooper[12] also gives figures for the design of absorption-oil heat-exchangers. These range from 12 to 16 sq. ft. per ɔoo gallons of oil per 24 hours. In general, the rate of heat exchange ‑ ıy apparatus used to cool gas-oil with water should be much more than when the same apparatus is used to transfer heat from hot ber-oil to colder saturated absorber-oil. The greater fluidity and :onductivity of water is not offset by the less fluidity of the gas-oil : cooler than in the exchanger. If the oil to be cooled were very ıs at the discharge temperature the foregoing statements would

Bull. 176, U. S. Bur. of Min., 34-6.
Day, "Handbook of the Petroleum Industry," Vol. I, p. 782.
"Handbook of the Petroleum Industry," Vol. I, p. 773.

not necessarily hold true. I am of the opinion that Cooper's allowances are more generous than necessary, and that Dykema's as given in Bulletin 176 are indefinite and possibly too low. In any event there is no excuse for talking in terms of units other than coefficients of heat transmission. The entire subject of coolers, and I should not omit condensers and exchangers, should receive attention by engineers versed in methods of accurate physical measurement.

In connection with fluid velocity the paper of G. A. Richter [13] will be found of interest and importance. Lucke [14] gives the value of H for various types of cooling and heat-exchanging apparatus handling aqueous solutions or water as 50-75 B.t.u. per hour per sq. ft. per 1° F.

In general, coolers should be constructed of small pipe rather than large, and fluid velocities should be as high as possible without requiring excessive pressure to force the fluids through the apparatus. Counter-current flow of the fluids will be used because the usual purpose of the cooler is to discharge the oil at the lowest possible temperature. The discussion of heat-exchangers that follows will be found applicable in no small measure to coolers.

Heat-Exchangers.

Double-pipe coils and tubular exchangers are the types most commonly used. These will be briefly described, and a few examples of performance cited.

The submerged pipe-coil is occasionally used as a heat-exchanger. For comparison with the other types of exchangers and also for comparison of heat transfer rates when this type of apparatus is used as a condenser or as a cooler I cite the following example. The exchanger consisted of a 6-in. pipe-coil, with a total external area of 1,896 sq. ft. placed in a tank 54 ft. in diameter and filled with 16° Bé. residuum to a depth of 17.5 ft. 500 barrels or 163,000 pounds per hour of crude oil flowed through the coil, and 85 per cent of this volume or weight of residuum flowed into and out of the tank. The crude entered the coil at 92° F. and left it at 118° F. The residuum entered the tank at 325° F. and left it at 283° F. 30.6° F. of the temperature lowering of the residuum was attributable to the cooling of the crude in the pipe-coil, and the balance to convective losses from the tank surfaces. The velocity of the crude oil in the pipe was 3.9 feet per second. The coefficient of heat transfer $H = 6.5$ B.t.u. per hour per sq. ft. per 1° F.

Tubular Exchangers.

The tubular heat-exchanger used in the Trumble plants is similar to the condenser shown in Figure 87. Baffles are so placed in the heads that one fluid makes four passes through the tubes. A baffle is also

[13] *Trans. Am. Inst. Chem. Eng.*, 12 (1919), Part II, pp. 147-85.
[14] *Eng. Thermodynamics*, p. 550.

placed between the tubes so that the other fluid travels from one end of the condenser to the other, and then back again. The construction is illustrated in Figure 90. The exchanger contains 180 18-ft. 2-in. tubes rolled into double tube-sheets. The external area of the tubes is 1,661 sq. ft. and the internal area 1,502 sq. ft.

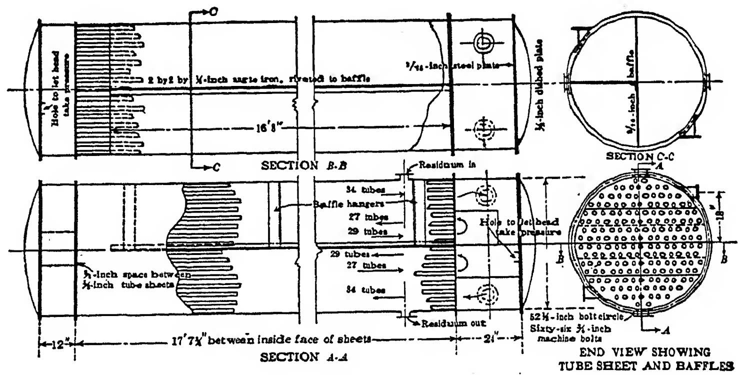


FIG. 90.—Tubular Heat-Exchanger Used in Trumble Plants.

The rate of heat transfer in tubular exchangers of this general design is such that H = 5 to 15 B.t.u. per hour per sq. ft. per 1° F. A value of H as low as 5 shows poor design or use under unfavorable circumstances, whereas a rate of exchange such that H = 15 can only be obtained if the fluid velocities are as high as is reasonably possible, and the oils of low viscosity. The average exchanger of the general design shown in Figure 90, when used to transfer heat from 18° to 22° Bé. residuum to crude, should be designed on a basis of H = 8 to 10. As these exchangers are frequently designed, the velocity of the residuum is 0.05 to 0.10 feet per second, and that of the crude 0.7 to 0.9 feet per second.

A somewhat different type of tubular exchanger, shown in Figure 91, is used at the Avon, California, refinery of the Associated Oil Company. The crude oil flows through the tubes at a velocity of 3.6 ft. per second, and the residuum in the space around the tubes at a velocity of 0.8 ft. per second. The rate of heat transfer is much higher than that in the Trumble exchangers, for H = 23 B.t.u. per hour per sq. ft. per 1° F.

The "multiwhirl" condenser and cooler that has already been shown in Figure 88 is easily adapted to use as a heat-exchanger.

The use of the Southwestern tubular sections as heat-exchangers has already been noted. The value of H ranges from 25 to 35 in practice.

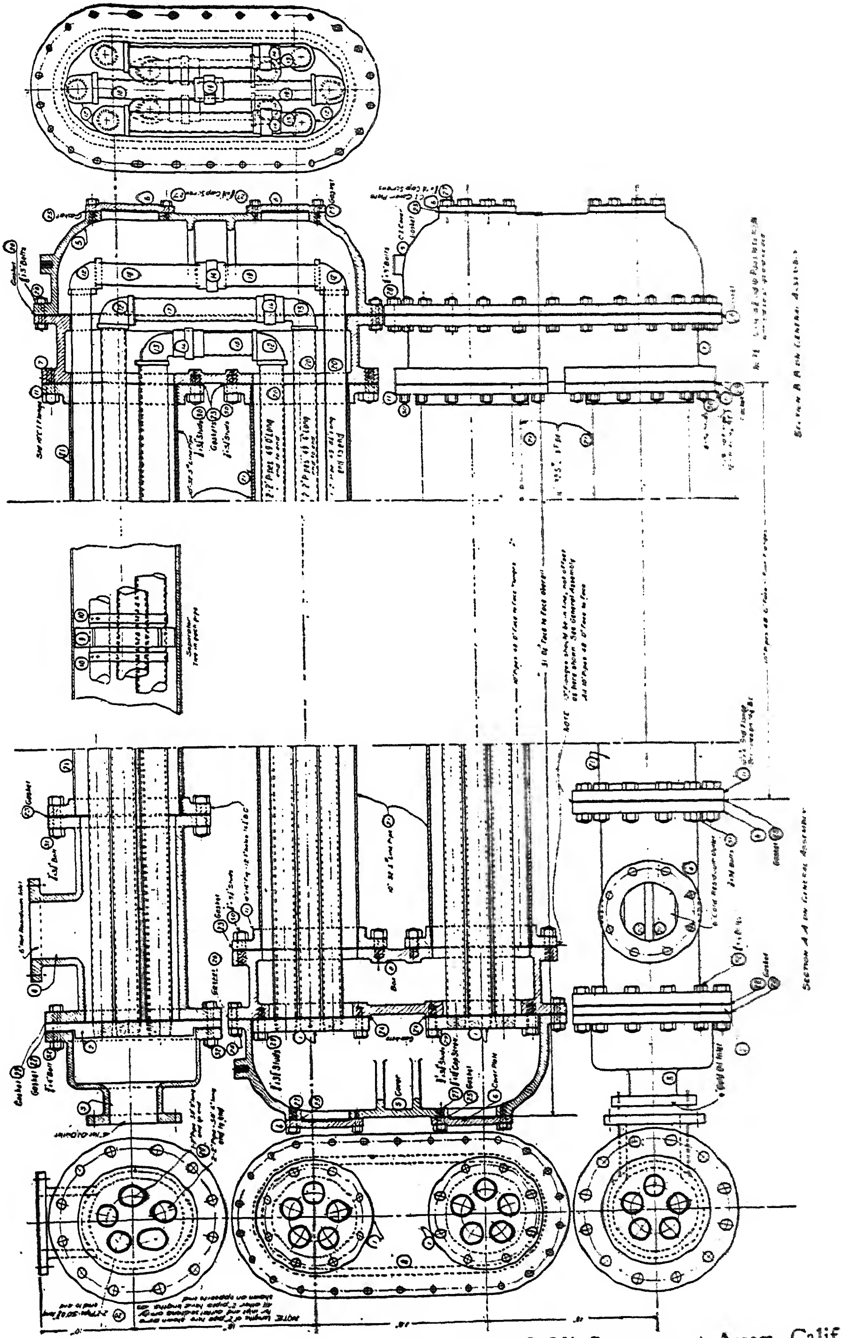
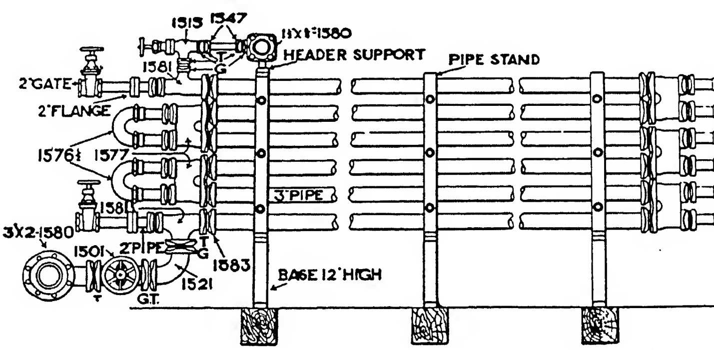


FIG. 91.—Heat-Exchanger Used by the Associated Oil Company at Avon, Calif.

Double-pipe Exchangers.

The double-pipe heat-exchanger has proved very satisfactory in service. This apparatus can be made by the use of ammonia fittings as shown in Figure 92, or all necessary joints and connections can be welded. The warmer fluid should flow in the annular space between the two pipes. The velocities of the two fluids should be as high as is feasible. If the oils are of the general nature of gas-oil, or somewhat more viscous, rates of flow up to 5 ft. per second will be found practical. If more viscous, rates of flow as low as 1 to 1½ ft. per second may be necessary. In this event the rate of heat transfer will be lowered. Values of H ranging from 10 to 20 B.t.u. per hour per sq. ft. per 1° F. should be used in design, the choice of the proper value depending on the type of oils and other conditions peculiar to the particular case. Usual allowance in absorption plant practice is 0.25 to 0.35 sq. ft. external surface of the inner pipe per gallon of oil flowing through the inner pipe per hour. In general 2-inch, 3-inch, or at most 4-inch pipe should be used for the inner coil, since this is favorable to rapid heat transfer. Under favorable circumstances values of H higher than 20 can be obtained.



Letters T or G indicate Tongue or Groove

FIG. 92.—Double-Pipe Heat-Exchanger.

A well designed heat-exchanger of the concentric pipe-coil type is the Hildebrand exchanger shown in Figure 93. This apparatus is made by the Hope Engineering and Supply Company. It consists of seven or more pipes, ranging from 1¼ in. to 8 in. in diameter, nested and bent into an elongated U. Welded cross connections at the ends of the pipes are so arranged as to permit counter-current flow of two fluids. The 8-in. 8-pipe exchanger, 72 feet long including bends, has 500 sq. ft. of heating surface, and is thus seen to be very compact. The over-all coefficient of heat transfer H is 50 to 55 B.t.u. per hour per sq. ft. per 1° F. depending on the particular service and conditions.

In a particular instance in which the Hildebrand exchanger is used to transfer heat from stripped absorber-oil to charged absorber-oil in an absorption plant for making natural gasoline, the data showing exchanger performance are as follows:

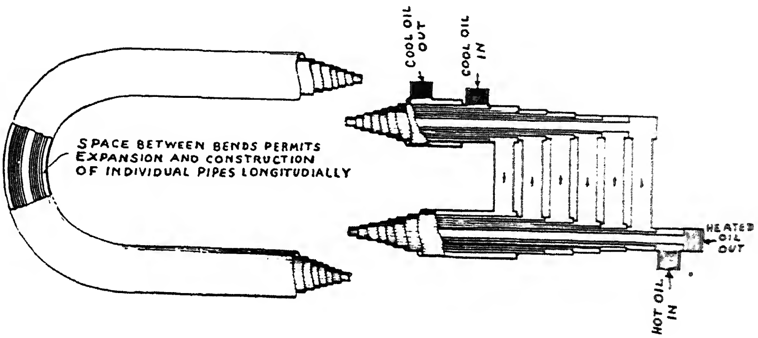


FIG. 93.—Hildebrand Heat-Exchanger.

Temperatures—

Stripped Oil to exchanger................	210° F.
Stripped Oil from exchanger............	106° F.
Charged Oil to exchanger................	93° F.
Charged Oil from exchanger.............	180° F.

Oil flowing through one exchanger 1750 gallons or 12,250 pounds per hour.
Total Surface—500 sq. ft.

From these data the values of the calculated quantities are found to be—

Mean temperature difference $\Theta_m = 20.4°$ F.
Over-all coefficient H = 56 B.t.u. per hour per sq. ft. per 1° F.

I am indebted to the Hope Engineering and Supply Company for these data.

Chapter VIII.

The Thermal Reactions of Hydrocarbons.

Knowledge of the thermal reactions of hydrocarbons is of special importance to the student of motor fuels in two separate fields of investigation and development, the manufacture of gasoline from heavy oils and residuums, and the burning of fuels in the cylinders of explosion and combustion engines. The first of these has received attention from many workers, but it has been recognized only recently that two sets of chemical reactions take place concurrently within the engine cylinders, one the oxidation reactions, and the other the dissociations and decompositions of the hydrocarbons. Strange as it may seem, present knowledge of hydrocarbon reactions is of greater help in understanding the changes within the engine cylinder than in formulating a rational theoretical background for the development of cracking processes. This is true even though the work of recent years has been undertaken mainly for the purpose of affording an understanding of cracking processes. Like most early investigation in a new field, it has been undertaken by those interested in obtaining results that should be of immediate application, and has therefore been somewhat empirical and lacking in thoroughness.

The scientific background for obtaining an understanding of the thermal reactions of hydrocarbons is to be largely attributed to the past importance of the subject as the basis of the manufacture of coal-gas, oil-gas, and carbureted water-gas. So it happens that by careful study a fairly accurate conception of the thermal reactions of the lower molecular weight hydrocarbons can be gained, but less can be learned of the reactions of the higher molecular weight hydrocarbons of paraffin or naphthene type.

Much of the lack of information regarding hydrocarbon reactions may be attributed to the difficulty of the work. Pure high molecular weight hydrocarbons can be obtained only with difficulty. The apparatus necessary for accurate study of thermal reactions must be designed so that temperature, pressure, and rate of feed of oil or hydrocarbon can be controlled with utmost precision. Materials exerting catalytic influences must not be used in the construction of the apparatus. All of this involves care and expense. Finally, satisfactory analytical methods for ascertaining exactly what products are obtained are yet to be developed. In particular the methods for estimating and identifying liquid olefin hydrocarbons are unsatisfactory. In fact none of the results of olefin determinations in the literature today can be accepted

as even approximately accurate. This subject is discussed elsewhere in this book.

Recognizing, then, that the incentive for careful study of some phases of subject has not long existed, and that unusual difficulties have been encountered in the work that has been done, we may proceed to consider the present status of knowledge of the thermal reactions of hydrocarbons. High molecular weight hydrocarbons may be decomposed under various conditions. Refinery technology today includes processes in which the oil in vapor form is passed through heated tubes, vapor phase processes in which catalysts are placed in the tubes, methods in which the oil is heated under pressure in stills, and methods in which the oil is distilled in the presence of substances such as aluminium chloride.

The products obtained in the several cases are not the same. The passage of the vapor of paraffin or naphthene hydrocarbons of 15 to 20 carbon atoms through tubes heated to 475° C. to 600° C. results in the formation of both lower molecular weight and higher molecular weight hydrocarbons. These products are highly olefinic. The gas produced at the same time is equivalent to 5 to 10 per cent of the original oil by weight, and contains 50 to 60 per cent of methane. When gas-oil is heated in a pressure-still low-boiling and high-boiling products are also produced, but the light distillate is less olefinic and the high-boiling portion richer in carbon than in the case of vapor-phase cracking. When gas oil is distilled with aluminium chloride the low-boiling distillate produced is only slightly olefinic. Obviously quite different reactions have taken place. The difference is probably not the result of temperature difference alone, for at temperatures of 360° C. to 400° C., such as are used in pressure-still processes and other liquid-phase processes, little chemical change occurs when gas-oil vapors are passed through a heated tube several hundred feet long. However, the time of heating involved in reactions in the vapor state is a matter of seconds, whereas in the methods involving reactions in the liquid state the time is a matter of minutes to hours. Also the molecular concentration in the liquid state is much greater than in the gaseous state. Further difference is probably attributable to the fact that in the one case we are dealing with reactions of gaseous molecules whereas in the other case the molecules compose a liquid. The surface layer of the hydrocarbon liquid is the seat of a force not ordinarily taken into account. This is the surface tension. The surface energy of the system tends toward a minimum, and this is probably a potent factor in the conversion of distillates such as gas-oil into the more volatil distillates which have lower surface tensions. In the discussion that follows the reactions of the hydrocarbons in the vapor state, and in those systems where liquid and vapor coexist, are treated separately.

For convenience in presentation the subject of the thermal reactions of hydrocarbons may be arbitrarily divided into three sections, first, the primary reactions, second, the secondary reactions or the chemical changes of the products of the first reactions, and third the reactions

of the simpler hydrocarbons such as ethylene, ethane, and methane. It is recognized that no such division as this exists in the reacting system, but that actually the changes taking place are in some measure interdependent, although the system is at no time in equilibrium.

The first comprehensive theory of hydrocarbon reactions was that of Berthelot.[1] Noteworthy as was the effort of this illustrious chemist, his conclusions are not in accord with most of those of later investigators. He confined himself to investigation of the reactions of the lower molecular weight hydrocarbons, methane, ethane, ethylene, acetylene, butylene, and amylene, and on this basis formulated a theory of hydrocarbon reactions that postulated, first, a decomposition or dissociation of the higher molecular weight hydrocarbons to those of low molecular weight, and second a synthesis of other higher molecular weight hydrocarbons from those of low molecular weight. Acetylene was considered one of the more important reacting substances.

Haber criticised Berthelot's work on the ground that so general a theory could not justly be built upon the results of limited experimentation, and that there was no justification for the conclusion that the larger hydrocarbon molecules break up immediately into hydrocarbons of low molecular weight. Furthermore, Berthelot believed that his hydrocarbon systems were in equilibrium, whereas it is now known that no hydrocarbon system comes to equilibrium at any time, with the possible exception of the system carbon-hydrogen-methane.

No writer or investigator other than Berthelot has attempted to formulate a general theory of hydrocarbon reactions that is based largely upon his own investigations. Not until June, 1916, when I published my dissertation on the "Decomposition of Hydrocarbons and Influence of Hydrogen in Carbureted Water-gas Manufacture"[2] was there a general review attempting to tie together into a comprehensive whole the work of numerous investigators, and to present in a single discourse the sequence and nature of the reactions involved when a high molecular weight hydrocarbon of paraffin or napthene type is thermally treated. This review by the writer was followed in December, 1916, by a similar presentation by E. L. Dunstan and F. B. Thole.[3] These writers also include a review of cracking processes.

Primary Reactions of High Molecular Weight Paraffin Hydrocarbons in the Vapor State.

When a high molecular weight paraffin hydrocarbon decomposes two simpler molecules both of these cannot be saturated hydro-ons unless carbon is formed at the same time.

[1] *Ann. Chim. Phys.*, 67, iii (1863), 53. *Compt. Rend.*, 62 (1866), 905, 947. *pt. Rend.*, 63 (1866), 788, 834. *Ann. Chim. Phys.*, 9, iv (1866), 413, 455. *. Chim. Phys.*, 12, iv (1867), 5, 122. *Bull. Soc. Chim.*, Paris, 2, vii (1867), *Ann. Chim. Phys.*, 16, iv (1869), 143, 148, 153, 162.

[2] Dissertation submitted in partial fulfillment of the requirements for the ree of Doctor of Philosophy in the Faculty of Pure Science, Columbia Uni-ity in the City of New York, 1916.

[3] *J. Inst. Pet. Tech.*, 3 (1916), 36-120. *J. Ind. Eng. Chem.*, 9 (1917), 879-908.

$$R_1CH_2CH_2CH_2R_2 \longrightarrow R_1CH_3 + CH_3R_2 + C$$

At low temperatures little, if any, separation of carbon takes place, so the reaction as above written is excluded.

The second possibility is that the high molecular weight paraffin may form two olefins as shown in the following equation:

$$R_1CH_2CH_2CH_2CH_2R_2 \longrightarrow R_1CH = CH_2 + CH_2 = CHR_2 + H_2$$

In this event hydrogen would be formed at low temperatures, but as a matter of fact low-temperature gases contain negligible quantities of hydrogen. An analysis of a typical gas formed at 621° C. is as follows:[4]

Hydrogen	10 per cent
Saturated Hydrocarbons (CH_4, C_2H_6)	38 per cent
Olefin Hydrocarbons (C_2H_4, etc.)	52 per cent

At still lower temperatures less hydrogen is formed.

The third possibility is the decomposition of the high molecular weight paraffin into olefin and paraffin. This may be represented

$$R_1CH_2CH_2CH_2R_2 \longrightarrow R_1CH = CH_2 + CH_3\,R_2$$

Experimental evidence indicates that this is the important mode of decomposition.

Vohl[5] believed that the higher paraffins decomposed into a paraffin of high molecular weight and an olefin of few carbon atoms. His views have not been accepted, and are not in accord with the larger portion of the experimental evidence recorded in the literature.

Prunier[6] found that propylene, butylene, amylene, and some crotonylene were among the products formed when "light petroleum vapors" were passed through a glowing tube.

The presence of amylene, hexylene, and a hydrocarbon believed to have been methylallene, $CH_3—CH = C = CH_2$, in the condensate obtained in Pintsch gas manufacture is reported by H. E. Armstrong.[7] One half of the condensate was found to be composed of aromatic hydrocarbons. The paraffins are not mentioned as having been found in the condensate, though the lower molecular weight paraffins constitute one half of the Pintsch gas.

A careful study of the hydrocarbons contained in Pintsch gas condensate, and in Pintsch gas tar, has been made by H. E. Armstrong[8]

[4] Dissertation of E. H. Leslie referred to above. Whitaker and Leslie, *J. Ind. Eng. Chem.*, 8 (1916), 593, 684.

[5] *Polytech. J.*, 177 (1865), 58-76.

[6] *Ber.*, 6 (1873), 72. *Ann. Chim. Phys.*, 5, 17 (1879).

[7] *J. Soc. Chem. Ind.*, 3 (1884), 462-68.

[8] *J. Chem. Soc.*, 49 (1886), 74-93.

and A. K. Miller.[9] They found the mono-olefins, amylene, n-hexylene, n-heptylene, ethylene, and propylene in the oil gases. No butylene nor homologues of higher molecular weight than heptylene were present. Only traces of paraffins were found in the tar, and these were not positively identified. Paraffins were not present in the condensate. The olefins were identified by oxidizing them with cold 4 per cent potassium permanganate and examining the organic acids formed.

L. M. Norton and C. W. Andrews[10] passed the vapors of normal hexane through a glass tube heated to a "bright red heat." The liquid products were condensed, and the gases were passed through absorption bottles, the first containing ammonical cuprous chloride and the others bromine dissolved in carbon disulfide. The products of the decomposition were amylene, hexylene, a compound C_4H_6, benzene, propylene, ethylene, and gases not absorbed by bromine. No acetylenes or butylenes were found. The evidence presented is not conclusive proof of the presence of hexylene in the liquid products.

The temperature of the tube was then lowered to a point at which the thermal reactions were not extensive. The products identified were propylene, butylene, amylene, hexylene, butine (C_4H_6), and gases not absorbed by bromine. The absence of ethylene is worthy of notice, but surely open to confirmation.

Isohexane at "red heat" gave products similar to those obtained from normal hexane.

Normal pentane decomposed more rapidly and completely than hexane. The products formed at "red heat" were ethylene, propylene, butine, traces of other unsaturated hydrocarbons, and gases not absorbed by bromine.

Brochet[11] identified n-butylene, n-amylene, n-hexylene, 1-3 butadiene, and piperylene in the compression liquids from Pintsch gas manufacture.

Tocher[12] studied the decomposition of octane, decane, and of several paraffin distillates. His work was directed toward determining the value of these materials for oil-gas manufacture, and though many data are given, there is little information bearing on the mechanism of the thermal decomposition. He says, however, that his results "bear out that at low temperature octane and decane are decomposed into ethylene and higher olefins, methane, and hydrogen, while at higher temperatures no higher olefins are formed, the gaseous products being simply ethylene, methane, and hydrogen."

Haber's[13] experiments led him to believe that when aliphatic hydro-rbons of more than two carbon atoms are heated at 600 to 800° C. a pical reaction takes place. Neither carbon nor hydrogen is formed

[9] *Chem. News*, 49 (1884), 285.
[10] *Am. Chem. J.*, 8 (1886), 1-9.
[11] *Compt. Rend.*, 114 (1892), 601-3.
[12] *J. Soc. Chem. Ind.*, 13 (1894), 231-237.
[13] *J. Gasbel*, 39 (1896), 377-82, 395-399, 435-439, 452-455, 799-805, 813-818, -834. *Ber.*, 29 (1896), 2691-2700.

directly, but a carbon-carbon bond breaks with formation of olefine and paraffin. Thus hexane would form amylene and methane. At lower temperatures, the hydrocarbon molecule breaks down in such a way that the olefin and paraffin are of more nearly equal size. At the higher temperatures the splitting out of methane predominates, though ethane may split off in small amount. At 500° C. hexane is not decomposed, but at 600 to 820° C. methane and amylene are the main products, along with gaseous olefins formed by decomposition of the amylene. Hydrogen is formed in small amount. In all cases in which higher hydrocarbons are heated at moderate temperatures to high temperatures, there is a combination of unsaturated residues to form higher molecular weight substances. An equilibrium condition is never reached.

The decomposition of a mixture of heptane and octane has been investigated by R. A. Worstall and A. W. Burwell.[14] The material used was a fraction (90 to 139° C.) from an Eastern petroleum. The thermal changes took place in a Pintsch gas retort heated outside to about 900° C. Careful examination of the gaseous and liquid products disclosed the presence of unchanged heptane and octane, but no lower molecular weight paraffins except methane, which was found in the gas. (In the light of later work, the absence of ethane in oil-gas of this type is open to question.) No naphthenes were present in the compression liquid or in the tars, but unsaturated hydrocarbons were present in large quantity, as were also the aromatic hydrocarbons, benzene, toluene, and the xylenes. The authors express the opinion that apparently no matter what hydrocarbon substances are used as a raw material, the products formed are qualitatively much the same.

Hempel[15] passed gas-oil vapor through an iron tube at temperatures of 700 to 800° C., and concluded from consideration of his gas analyses that the groups splitting off were chiefly those of one or two carbon atoms. The decomposition into methane and high molecular weight olefins must predominate because of the high content of methane in the gases obtained. Hempel's views are essentially in accord with Haber's.

In order to determine the temperature at which paraffin hydrocarbons, when heated in vapor form, start to evolve hydrogen, Engler and Spanier[16] slowly passed fractions of an American kerosene through a glass tube 80 cm. long and 2.4 cm. in diameter. The oil had been treated with sulfuric acid to remove the olefins. The results are of very real interest, and are presented in Table LI.

The formation of hydrogen during the passage of these higher paraffins at a rate of 0.6 to 0.8 cc. per minute through the heated tube described begins at a temperature of 470 to 480° C. The formation of gaseous olefins is less the lower the temperature. The gaseous paraffins, mainly methane, compose the larger part of the gases formed at the lower temperatures.

[14] *Am. Chem. J.*, 19 (1897), 815-845.
[15] J. Gasbel, 53 (1910), 53-58, 77-83, 101-105, 137-141, 155-165.
[16] *Das. Erdol*, Vol. I, 574-5.

TABLE LI

THERMAL TREATMENT OF FRACTIONS FROM AMERICAN KEROSENE

Fractions 150 to 180° C.
C_9H_{20}–$C_{11}H_{24}$

Temperature °C.	Oil Used ccm.	Time of Entire Run Minutes	Oil Recovered ccm.	Gas ccm.	Composition of the Gas on Air-free Basis		
					Unsaturated	Saturated	Hydrogen
450-460 ...	35	45	32	750	8.0	91.4	0.0
460-470 ...	35	45	33	850	10.5	89.5	0.0
470-480 ...	35	45	33	850	17.8	82.2	0.0
480-490 ...	35	45	33	1100	19.7	78.3	1.9
490-500 ...	35	45	33	1100	39.1	56.9	4.0

Fractions 200 to 230° C.
$C_{11}H_{24}$–$C_{13}H_{22}$

Temperature °C.	Oil Used ccm.	Time of Entire Run Minutes	Oil Recovered ccm.	Gas ccm.	Composition of the Gas on Air-free Basis		
					Unsaturated	Saturated	Hydrogen
460-470 ...	50	71	48	400	14.4	85.6	0.0
470-480 ...	39	66	36	600	30.8	67.7	1.5
480-490 ...	28	40	23	1100	46.6	50.3	3.0
470-480 ...	21	33	..	....	31.2	67.0	1.9

Fractions 250 to 280° C.
$C_{14}H_{30}$–$C_{16}H_{34}$

Temperature °C.	Oil Used ccm.	Time of Entire Run Minutes	Oil Recovered ccm.	Gas ccm.	Composition of the Gas on Air-free Basis		
					Unsaturated	Saturated	Hydrogen
450-460 ...	50	65	48	850	23.5	76.4	0.0
460-470 ...	43	60	41	850	32.6	67.3	0.0
470-480 ...	34	50	33	1050	39.0	59.3	1.7
480-490 ...	39	55	36	1200	44.5	53.0	2.5
460-470 ...	31	45	30	900	36.9	62.9	0.0

Examination of the liquid products showed results of which the following are typical:

	Unsaturated Hydrocarbons in Recovered Oil (Temp. of Furnace 470 to 480° C.)
	Per Cent
Heptane (B. P. 98° C.)	4.4
Fraction 150-180° C.	17.8
Fraction 200-230° C.	30.8
Fraction 250-280° C.	19.0

Experiments were performed in which heptane and octane were passed through the tube furnace in the same manner as the fractions from American petroleum. The results are shown in Table LII.

TABLE LII

Material	Temperature	Oil Used ccm.	Time of Entire Run Minutes	Gas Formed ccm.	Composition of the Gas on Air-free Basis		
					Unsaturated	Saturated	Hydrogen
Heptane	470-480 ..	10	24	70	1.5	98.5	0.0
	480-490 ..	10	20	70	1.4	97.7	0.9
Octane	460-470 ..	10	30	70	1.4	98.6	0.0
	470-480 ..	10	30	70	1.9	97.5	0.6
	480-490 ..	10	30	100	1.7	97.5	0.8

When heptane was treated similarly in another set of experiments, the following amounts of hydrogen were found in the gases formed:

	Per cent Hydrogen
480-490° C.	3.6
500-510° C.	3.9
520-530° C.	10.2

The work of Engler and his collaborators is a substantial contribution to the understanding of the early stages of the decomposition of the paraffin hydrocarbons in the vapor state. It substantiates Haber's conception that the first reaction is a decomposition into low molecular weight paraffin and higher olefin.

The decomposition of hexane was studied by Ipatiev and Dowgelevitsch.[17] They heated the hydrocarbon under ordinary pressure to 660 or 710° C. The time of treatment was 2 hours or 2½ hours, a period so long that their results are of little value as indicating the nature of the reactions of primary decomposition. Ethylene, propylene, and probably isobutylene were present in the gases formed. The liquid products contained hexane, but no other paraffin, small amounts of olefins, and other substances not identified.

A compression liquid from Pintsch gas manufacture was examined by B. T. Brooks,[18] and found to contain 48 per cent of olefins removable by cold concentrated sulfuric acid.

According to Hall, the mode of decomposition of a long chain paraffin hydrocarbon depends on temperature and pressure. An increase in pressure greatly diminishes the yield of fixed gases, i.e., methane and ethane. At 560° C. a change of 20° C. in temperature makes a dif-

[17] *Ber.*, 44 (1911), 2987.
[18] *J. Fr. Inst.*, 180 (1915), 653-673.

ference of 50 per cent in gas production, and a difference in the gravity of the liquid distilling below a given point, the greatest difference being in the unsaturated portion. A change of 40° C. in temperature results in a 40 per cent difference in production of olefins. Distillates containing from 30 per cent to 90 per cent unsaturated hydrocarbons can be produced by changing no other condition than temperature.

The most exact work on the separation of the hydrocarbons resulting from the decomposition of the hydrocarbons of high molecular weight is that of Burrell, Seibert, and Robertson. By a series of careful fractionations at low temperatures, these investigators have determined the percentages of the various components in Pittsburgh coal gas and water gas. Table LIII shows their results.

TABLE LIII

ANALYSIS OF PITTSBURGH COAL- AND WATER-GAS

Carbon dioxide	1.4	4.8
Oxygen	0.7	(a)
Carbon monoxide	7.9	29.8
Hydrogen	50.6	32.0
Methane	31.1	13.1
Ethane	0.9	2.9
Ethylene	2.1	9.8
Propylene	0.3	2.8
Butylene	0.1	1.7
Butane	0.0	0.0
Propane	0.0	0.3
Benzene (b)	1.4	1.5
Nitrogen	3.5	1.3
	100.0	100.0

(a) Results calculated to air-free basis.
(b) Benzene or vapor having an inappreciable pressure at 78° C.

The notable feature of these results, so far as their bearing on the primary decomposition of hydrocarbons is concerned, lies in the fact that the percentages of olefins were always higher than the percentages of paraffins of the same number of carbon atoms. Thus, in water gas there was 2.8 per cent propylene, but only 0.3 per cent propane, and 1.7 per cent butylene, but only traces of butane. With the relative thermal stability of these hydrocarbons in mind, it is seen that these results are in accord with the view that the primary thermal decomposition of the paraffin hydrocarbons of high molecular weight results in the formation of methane and ethane along with higher molecular weight olefins.

G. Egloff, T. Twomey, and R. J. Moore,[19] studied the thermal decomposition of a paraffin-base gas-oil that distilled between 200° C. and 350° C. The oil was passed through a heated steel pipe 8 inches

[19] *Met. Chem. Eng.*, 15 (1916), 523-529.

in diameter, and 11 ft. 6 in. long. Time of heating and temperature were varied, while the pressure was held constant at 150 lbs. gage. They were particularly interested in the formation of aromatic hydrocarbons, but the olefins were determined in the distillation cuts from the recovered oil. The sulfuric acid method was used for these determinations. The content in the larger number of cuts was between 20 per cent and 40 per cent. When it is recalled that the sulfuric acid method for determining olefins always gives low results, and may not indicate one half of the olefins actually present, it is evident that the decomposition of the paraffin hydrocarbons of this oil results in the formation of a large proportion of olefins.

In an investigation similar to the last above Egloff, Twomey, and Moore [20] studied the effect of temperature and time of heating on the formation of gasoline from a Pennsylvania crude oil. The gasoline was recovered from the oil before the latter was thermally treated. The olefins, determined by the sulfuric acid method, were present in the gasoline cut (distillate to 150° C.) to the extent of 22.0 per cent to 29.0 per cent.

A paper by Egloff and Twomey [21] reports their work upon the effect of temperature on the formation of olefins from Pennsylvania petroleum at ordinary pressure. The recovered oils were distilled, and the olefins determined in the several cuts by the sulfuric acid method. The percentage of olefins varied from one to fifty-one.

The thermal stability of the paraffin hydrocarbons has been investigated by G. Egloff and R. J. Moore.[22] They call attention to the fact that it is generally believed that the higher the molecular weight of the paraffins, the less the thermal stability. Statements such as, "It is well known that the simpler petroleum hydrocarbons are stable at much higher temperature than those of higher molecular weight" [23] are found frequently. Egloff and Moore claim to have shown that the general impression of the order of stability of the paraffin hydrocarbons is incorrect, and that in fact the hydrocarbons, $C_{12}H_{26}$ and $C_{15}H_{32}$, are most stable, and those of fewer and of more carbon atoms less stable. A Pennsylvania paraffin-base petroleum was fractioned into cuts with the temperature limits (1) to 150° C., (2) 150-200° C., (3) 200-250° C., (4) above 250° C. The fourth fraction was distilled under a vacuum into two cuts. Each of these fractions was passed, 200 cc. per hour, through a tube furnace heated electrically to 700° C. The results as presented by the authors are shown in Table LIV.

These results show that the hydrocarbons from Pennsylvania petroleum boiling from 200 to 250° C. and of empirical formula, $C_{12}H_{26}$ to $C_{15}H_{32}$, are more stable when heated than the lower boiling paraffins or the higher boiling paraffins. The hydrocarbons boiling above 250° C. are much less stable thermally than those boiling below 200° C.

[20] *J. Ind. Eng. Chem.*, 8 (1916), 1102.
[21] *Met. Chem. Eng.*, 14 (1916), 247-50.
[22] *Met. Chem. Eng.*, 16 (1917), 47-51.
[23] Bacon and Hamor, "American Petroleum Industry," Vol. II, 558.

TABLE LIV

RESULTS OF THERMAL TREATMENT OF FRACTIONS FROM PENNSYLVANIA PETROLEUM

Original Oil Fraction	A to 150° C.	B 150-200° C.	C 200-250° C.	D Vacuum 150-200° C.	E Vacuum 200-250° C.
Per cent of original oil recovered	2.3	29.3	66.7	25.0	20.0
Per cent of original oil converted into gas and carbon	97.7	70.3	33.3	75.0	80.0
Difference between sp. gr. of original oil and recovered oil	0.053	0.027	0.008	0.047	0.120
Difference between refractive indices of original oil and recovered oil	0.03507	0.01805	0.00699	0.0173	0.03556
Liter of gas formed per liter of oil treated	710.2	560.7	420.4	476.7	514.4
Per cent benzene in recovered oil	3.1	1.2	0.8	8.4	14.4
Per cent toluene in recovered oil	1.3	3.8	1.0	2.8	10.0
Per cent xylenes in recovered oil	2.2	2.7	2.0	2.5	11.1

Egloff and Moore determined the per cent of unsaturation in distillation cuts from the recovered oils. The results were inconsistent.

The conclusions of these investigators should be confirmed by further studies in which the paraffin hydrocarbons are used, or at least distillates that have been shown to be entirely composed of paraffin hydrocarbons. The sections in the book on the composition of Appalachian petroleums should be referred to in this connection.

SUMMARY.

'mary Thermal Reactions of High Molecular Weight Paraffin Hydrocarbons in the Vapor State.

Though it must be admitted that the experimental evidence is limited and none too satisfactory in character, the indication is that the first reaction in the thermal decomposition of a high molecular weight paraffin hydrocarbon in the vapor state results in the formation of a long chain olefin and a gaseous paraffin. Otherwise it is difficult to explain the presence in the reaction products of higher olefins, and

the absence of paraffins of equal number of carbon atoms. The composition of oil-gases made at low temperatures is confirmatory. These gases always contain 35 to 40 per cent of methane and ethane, approximately 10 per cent of hydrogen, and 45 to 55 per cent of gaseous olefins. The presence of ethylene and propylene in these gases may be brought forward as an argument against the belief that the primary reaction is as given above, but it is probable that the ethylene and propylene are formed by the secondary decomposition of the higher olefins. Moreover, if the primary reaction were a scission into long chain paraffin and low molecular weight olefin, it would be difficult to account for the fact that the high molecular weight paraffins are not found in the reaction products along with the higher olefins. In this connection, it should be recalled that estimations of "olefins" in cracked distillates have usually been made by the sulfuric acid method, and are in error to a variable extent, probably often as much as 100 per cent. The effect of temperature and pressure on the primary reactions is yet to be ascertained, and, in fact, the exact effect of temperature change would be most difficult to determine, since the result would be masked by secondary reactions.

The thermal stability of the paraffin hydrocarbons varies with molecular weight. Many more data are needed before this question can be regarded as entirely settled, but in the light of the experiments of Egloff and Moore already cited, it appears that the hydrocarbons $C_{12}H_{26}$ to $C_{15}H_{32}$ are most stable. Those of fewer carbon atoms are less stable and those of higher molecular weight still less stable.

The notable feature of many investigations, so far as their bearing on the primary decomposition of hydrocarbons is concerned, lies in the fact that when reaction products were examined the percentages of olefins were always found to be higher than the percentages of paraffins of the same number of carbon atoms. Thus in water gas there was 2.8 per cent propylene but only 0.3 per cent propane, and 1.7 g. butylene, but only traces of butane. With the relative thermal stability of these hydrocarbons in mind it is seen that these results are in accord with the view that the primary thermal decomposition of the paraffin hydrocarbons of high molecular weight results in the formation of methane and ethane along with higher molecular weight olefins.

Thermal Reactions of the Cyclic Hydrocarbons Other than the Aromatics.

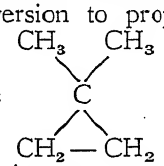
The commoner cyclic hydrocarbons, other than the aromatics, are the polymethylenes and the naphthenes. The nomenclature by which the former are designated is more commonly understood than that of the naphthenes. The latter, strictly speaking, are the monocyclic hexahydroaromatic hydrocarbons such as hexamethylene, hexahydrotoluene, hexahydroxylenes, hexahydromesitylene, or hexahydrocymene. The term naphthene is loosely used, however, to designate cyclic hydrocarbon compounds, and particularly those found in various petroleums.

This broader usage is to be deprecated since even our limited knowledge of a few classes of these hydrocarbons indicates that their thermal reactions, to say nothing of all other properties, are different. Furthermore, as knowledge accumulates, strict nomenclature will be necessary if confusion is to be avoided.

In the following paragraphs the present very limited knowledge of the thermal reactions of various cyclic compounds is reviewed. This résumé is included at this point, since, in part, the products formed from certain of the cyclic hydrocarbons are olefins, and the discussion, therefore, roughly parallels that of the primary thermal reactions of paraffin hydrocarbons.

Russian petroleum has been decomposed in a Patterson oil-gas retort by V. B. Lewes.[24] The tars obtained were composed of olefin, paraffin, and aromatic hydrocarbons. The individual hydrocarbons, with the exception of benzene, were not identified.

W. Ipatiev and W. Huhn[25] have shown that cyclopropane when slowly passed through a tube heated to 360 to 370° C. isomerizes to a slight extent to propylene. If the tube is filled with an aluminium oxide catalyst, a 15 per cent conversion to propylene takes place. Similarly the dimethyl cyclopropane



is changed to trimethylethylene. These reactions are in contrast to those of the more stable five- and six-carbon ring-compounds.

C. Engler and L. Rosner[26] cracked a Baku petroleum with the result that they obtained 78 per cent recovered distillate and 12 per cent coke. The gas formed represented 10 per cent of the volume of the original oil. The composition was as follows:

	Per Cent
Carbon Dioxide	0.6
Unsaturated Hydrocarbons	12.0
Oxygen	1.0
Carbon Monoxide	2.2
Hydrogen	8.8
M[illegible]ane	43.0
[illegible]ne	31.6
[illegible]ogen Sulfide	0.6
	100.1

The large proportion (74.6 per cent) of saturated hydrocarbons in this gas is of interest when compared to the 35 to 45 per cent ordinarily

[24] *J. Soc. Chem. Ind.*, 11 (1892), 585-590.
[25] *Ber.*, 36 (1903), 2014-16.
[26] *Chem. Rev. d. Fett u. Harz Ind.*, 13 (1906), 144.

found in the gases formed during the cracking of a paraffin-base oil in the vapor state.

The reactions of hexamethylene when heated with or without pressure, and with or without the presence of aluminium oxide as a catalyst, have been studied by W. Ipatiev and N. Dowgelewitsch.[27] This hydrocarbon proved to be much more stable than hexane. When hexamethylene was heated at ordinary pressure, the gaseous products formed at 750° C. were 14.0 per cent hydrogen, 44.5 per cent olefins, and 42.0 per cent saturated hydrocarbons. The liquid products contained undecomposed hexamethylene, small amounts of olefins, and other hydrocarbons that did not react with a nitrating acid mixture nor with potassium permanganate. Aluminium oxide catalyzed the reaction to a moderate extent. The decomposition under pressure was much more violent, and at 510° C. and 100 to 110 atmospheres pressure, olefins (5 to 10 per cent) aromatic hydrocarbons, and polymethylene hydrocarbons were found in the liquid products. The presence of methyl-pentamethylene in the products was demonstrated, but the isomerization of hexamethylene to this compound takes place only under high pressure.

N. Zelinski[28] has shown that in the presence of palladium black or platinum black hexamethylene and methyl-hexamethylene are dehydrogenated. The reaction begins at 170° C. and has a maximum velocity at 300° C. At 100 to 110° C. benzene may be easily hydrogenated. The dehydrogenation of the cyclohexanes by palladium or platinum black is apparently specific. Hexane, pentamethylene, and methyl-pentamethylene are not affected at 170 to 300° C.

N. Zelinsky and F. A. Herzenstein[29] passed a mixture of equal parts of methyl-pentamethylene and hexamethylene over platinum black at 300° C. The hexamethylene was almost quantitatively dehydrogenated to benzene while the methyl-pentamethylene was unaffected. Methyl-hexamethylene dehydrogenates under similar conditions yielding toluene and hydrogen. Another cyclic hydrocarbon present in a naphtha fraction from Baku petroleum, and of nearly the same boiling point as methyl-hexamethylene, was unaffected by passage over the platinum-black catalyst. Ultimate analysis showed it to be of the empirical formula C_nH_{2n}, but evidently it was not a cyclohexane.

The thermal reactions of cyclohexane, methylcyclohexane and di- and tetra-hydronaphthalene have been investigated by D. T. Jones.[30] The decomposition was carried out in a glass bulb filled with broken porcelain that had been heated to 520° C. and from which, during the heating, the air had been evacuated. The hydrocarbon was introduced in a glass capsule, and the bulb heated slowly in a small electric resistance-furnace. The decomposition of all the substances except di-hydronaphthalene began at 490 to 510° C., and of the di-hydro-naphthalene at

[27] *Ber.*, 44 (1911), 2987-2992.
[28] *Ber.*, 44 (1911), 3121-3125.
[29] *Ber.*, 45 (1912), 3679-81.
[30] *J. Chem. Soc.*, 107 (1915), 1582-1587.

390° C. The gases were analyzed and found to contain slightly over 40 per cent hydrogen in the case of the cyclohexane, and over 80 per cent in the case of the hydro-naphthalenes. This is in contrast to the hydrogen content of gases evolved during the low temperature decomposition of the paraffin hydrocarbons. The gases from the cyclohexanes also contain olefins, benzene, methane, and ethane. The liquid and solid products were not examined in an exhaustive manner, but were shown to contain benzene when cyclohexane was decomposed, and much naphthalene when the hydro-naphthalenes were decomposed. The results indicate that these hydrocarbons generally retain in some measure their aromatic properties. The somewhat modified character is shown by the formation of ethylene, methane, and ethane that involves a scission of a —C—C— bond.

G. Egloff, T. Twomey and R. J. Moore [31] studied the decomposition of two naphthene-base oils. The vaporized oils were passed through a steel tube heated electrically over 18 in. of its length. The oil was fed to the vaporizer at the rate of 246 grams per hour. Temperatures of 550° C., 600° C., 650° C. and 700° C., and pressures of one and of eleven atmospheres were used. The recovered oils contained varying percentages of olefin, aromatic, and saturated hydrocarbons. The authors comment on the markedly different results obtained from the two oils under the same experimental conditions. At 11 atmospheres pressure and 650° C. one of the oils yield 18.2 per cent of its volume of combined benzene, toluene, and xylene. This is in contrast to the formation of only 12.7 per cent of aromatics from a paraffin-base oil treated under the same conditions.[32]

The relative stability of the hydrocarbons of the polymethylene series is discussed by W. Hückel.[33] These hydrocarbons cannot be regarded as forming an homologous series in the same sense as the paraffins or olefins. The heat of combustion of a CH_2 group is different in every ring. Ethylene may be regarded as a two-atom member of the ring-series. Ethylene, trimethylene, tetramethylene, pentamethylene, and hexamethylene require increasing amounts of energy for the rupture of their —C—C— unions. The value of the heat of combustion of a —CH_2 group in the several hydrocarbons is as follows:

	Calories
Ethylene	170
Trimethylene	168.5
Tetramethylene	165.5
Pentamethylene	159.0
Hexamethylene	158.0
Paraffin Hydrocarbon	158.0

[31] *Met. Chem. Eng.*, 15 (1916), 387-393.
[32] *Met. Chem. Eng.*, 15 (1916), 523-529.
[33] *Ber.*, 53, B (1920), 1277-83.

Reference is made to the work of K. Fajans.[34]

A series of experiments has been carried out by the writer in which distillates of 38° Bé. from mixed California crude oils were passed through a 2-in. steel tube 200 ft. long heated to various temperatures in a gas-fired furnace. The rate of oil-flow was carefully controlled, and one volume of water was introduced with every eight volumes of oil. The pressure on the system was eighty pounds gage. Temperatures were measured by means of a thermocouple so placed that it measured the temperature of the gaseous reaction mixture as it exited from the tube.

The work was designed to study the value of the distillates as raw materials for the production of cracked-gasoline, and the results were therefore of a rather empirical nature. However, they have some scientific value.

The treated oils were distilled in the laboratory. The specific gravity of each fraction was taken, and the "unsaturation" of the fraction distilling below 305° F. was determined by the sulfuric acid method.

At 582° C., feed-rate of one gallon per minute, and pressure of 80 lbs. gage the following results were obtained:

Distillate	% Distilling under 305° F.	Sp. Gr. 60/60 of Cut to 305° F.	Unsaturation
38° Bé.	10.0	0.7491	46.0
32° Bé.	32.0	0.7818	40.0

These results are representative of data too voluminous for presentation in detail. The large proportion of olefins produced from a cyclic-base oil is of interest. The unsaturation as given is probably far below the actual olefin content, since the sulfuric acid method was used to determine these substances. The analysis of a typical gas produced in the above experiments is also significant:

	Per Cent
Unsaturated Hydrocarbons	16
Hydrogen	15
Methane	57
Ethane	10
CO_2, CO and N_2.	2
	100

The large proportion of ethane and methane is interesting, and is comparable to the 74.6 per cent of these gases found by Engler and Rosner in the gas produced during the cracking of a Baku petroleum. The above gas analysis is quite in contrast to a typical analysis of the

[34] *Ber.*, 53, B (1920), 643-65.

gas found when a paraffin-base kerosene distillate is cracked under generally similar conditions:

	Per Cent
Unsaturated Hydrocarbons	30.5
Hydrogen	9.3
Methane	45.1
Ethane	11.5
CO_2, CO, and N_2	3.6
	100.0

The distribution of the olefins in the distillate obtained up to 305° F. is given below. 500 cc. of this distillate was fractionated through a Glinsky head, and the specific gravity and unsaturation determined for the cuts indicated.

	Temp. ° F.	Sp. Gr. 60/60° F.	Unsaturation
1st 10%	174	0.7046	62
2nd 10%	199	0.7396	56
3rd 10%	220	0.7634	52
4th 10%	250	0.7795	46
5th 10%	302	0.7914	44
6th 10%	323	0.8037	40
7th 10%	384	0.8211	38
8th 10%	425	0.8419	34

These results do not prove that the olefin percentages are really higher in the low boiling portions than in the higher boiling cuts, for it is now known that many of the higher olefins do not readily react with sulfuric acid. The most interesting feature of these experiments is the large proportion of unsaturated compounds formed when an oil of cyclic-base is thermally treated under conditions that bring about primary chemical change without extensive secondary reactions. The nature of these unsaturated hydrocarbons is not known.

The reactions of the methylenes and naphthenes when thermally treated in the liquid state is discussed in sections that follow.

SUMMARY.

ıt knowledge of the thermal reactions of the cyclic hydro-
er than the aromatic hydrocarbons is so limited as to make
e to gain any broad conception of the subject. Apparently
hylenes of less than five carbon atoms tend to rearrange to
s. The five and six carbon ring compounds are the most
ler pressure it is probable that the hexamethylenes rearrange,
part, to form the more stable pentamethylenes. The hexa-
dehydrogenate readily at 300° C. in the presence of plati-

num or palladium black to form aromatic hydrocarbons. The indications are that dehydrogenation takes place without a catalyst at temperatures over 600° C., for the petroleums of cyclic-base yield large quantities of benzene, toluene, and xylenes when treated thermally above this temperature. The pentamethylenes dehydrogenate less readily than the hexamethylenes.

The mechanism of the more extensive thermal-decomposition of these cyclic compounds, in which olefins and paraffins as well as aromatics are products, is not understood. In the case of those compounds in which one or more of the hydrogen atoms of the nucleus is replaced by long paraffin side-chains it is reasonable to suppose that the side-chains react in a manner analogous to that of the paraffins themselves. This is pure speculation, however, for it has not been experimentally demonstrated.

The large proportion of olefins produced when cyclic-base petroleum distillates are thermally treated at temperatures between 550° C. and 600° C. are of interest, but at present our knowledge of the chemistry of these changes is very limited.

Thermal Reactions of Liquid Hydrocarbons.

I have indicated in the introduction to this chapter that there are fundamental differences in the results obtained when hydrocarbons are thermally treated in the vapor state and when they are treated in a manner such that both liquid and vapor are present.

The temperature of treatment of liquid-vapor hydrocarbon systems is moderate, ranging usually in commercial practice from 350° C. to 450° C. As a consequence of this the effect of secondary reactions is less than in vapor-phase systems, and the tertiary reactions, that is, reactions of the simple gaseous hydrocarbons that are formed, are of small consequence. Accordingly I have chosen to discuss this subject separately and following my review of primary reactions in the vapor state.

The first suggestion that oils were chemically altered by heating was made by Professor Silliman of Yale in April, 1855. His original memoir as then written for Messrs. Eveleth, Bissel and Reed as a "Report on the Rock Oil, or Petroleum, from Venango Co., Pennsylvania," was later published.[35] This document is the classic of petroleum literature.

In 1865 a patent was taken out by Young[36] covering the treatment of oil under 20 lbs. pressure, for the purpose of increasing the yield of burning-oil. This was followed in a few years by an investigation of the effect of heating paraffin in a sealed tube.[37] The paraffin used was a purified product from shale oil. It solidified at 43° C., melted at 46° C., and had a specific gravity of 0.906 at 13° C. Ultimate

[35] *The Am. Chem.*, 2 (1872), 18-23.
[36] English Patent No. 3345 (1865).
[37] *Proc. Roy. Soc.*, 19, 370; 20, 488; 21, 184 (1871-1873).

analysis showed C = 85.14 per cent, H = 14.81 per cent. When heated in a sealed tube placed entirely within the furnace decomposition did not take place, but when heated in a V-shaped tube, one leg in the furnace and the other outside, six distillations rendered the paraffin completely liquid. In comparison to this it was found that a paraffin oil boiling at 225° C. was unaffected by the same treatment. The lesser stability of the higher molecular weight paraffins was thus indicated.

Three and one-half kilograms of paraffin distilled in a larger apparatus in such manner that the pressure in the vessel was 20 to 25 pounds yielded from liters of liquid products. Fractional distillation of this material showed the following results:

Distillate	Per Cent
Below 100° C.	7.5
100-200° C.	25.0
200-300° C.	67.5

These fractions were further distilled until the liquid, in large part, collected into fractions as indicated in the table below. These cuts were carefully treated with bromine, and the properties and composition of the addition compounds and of the non-reactive hydrocarbons determined. The indicated composition is given in the table.

Boiling Point of Fraction ° C.	Hydrocarbons Contained in the Fraction
32-38	Amylene, pentane
65-70	Hexylene, hexane
94-97	Heptylene, heptane
122-125	Octylene, caprylidene, octane
145-148	Nonylene, nonane
170-172	Decylene, decane
192-197	Undecylene, undecane
212-215 230-235 252-255 273-276 290-295	Mixtures of olefins and paraffins

These investigators stated that they were unprepared to offer an explanation of the mechanism of the decomposition of the paraffin hydrocarbons.

S. F. Peckham [38] reports the distillation of four crude oils under pressure. The oils originally contained 2.5 to 20 per cent of burning oil. The yield of crude burning oils after two distillations at 35 to 40 lbs. pressure was from 29.1 to 62.7 per cent. The chemical nature of the products produced by the cracking was not studied.

[38] *Am. J. Sci.* (2), 47 (1869), 9-16.

A pressure-still distillate made from a heavy brown-coal tar oil was examined by Engler and Schneider.[39] The distillate was found to contain the paraffins from pentane to nonane, and probably naphthenes. One-third of the distillate was composed of olefins as shown by treatment with concentrated sulfuric acid. Benzene, mesitylene and pseudo-cumene, were also identified.

R. Zaloziecki [40] expresses the opinion that the polymethylenes other than the stable hexamethylenes undergo an isomeric change into olefins when heated in a sealed tube to temperatures of 250° C. The paraffins are apparently not affected under these conditions.

Engler and Jezioranski [41] distilled a Galician crude oil residue (b. p. 200° C. and over) at ordinary pressure. The decomposition started at 200° C. and at the same time polymerization of the smaller decomposition products occurred. As the temperature increased the nature of the reactions changed so that the lower paraffins and higher olefins were formed. Later methane and ethylene were evolved, and finally hydrogen and methane. The light distillate produced contained 41 per cent unsaturated and 59 per cent saturated hydrocarbons as shown by treatment with sulfuric acid. The percentage of olefins increased from 23 to 48 per cent with rise in boiling point. The residue from the distillation, equal in volume to one quarter of the original oil, was rich in carbon and low in hydrogen. (Residue from distillation at ordinary pressure: C = 88.2 per cent, H = 11.2 per cent.)

The composition and nature of a cracked oil from a Galician refinery has been studied by Engler and Grüning.[42] The oil distilled mainly between 200 and 400° C. The fractions were treated with concentrated sulfuric acid, and with fuming acids of 2½ per cent and 5 per cent excess SO_3. Concentrated sulfuric acid removed 11 to 21.5 per cent of the various fractions, the amount removed increasing with the boiling point of the fractions. The 5 per cent fuming acid removed 17.5 to 38.5 per cent. The oil residue after treatment with acid was lower in carbon and higher in hydrogen content than the fraction before treatment, and this difference was more marked in the higher boiling fractions. The elementary composition of the treated fractions lay between that of the olefins and that of the paraffins. The investigators believed that the portion of the oil unaffected by sulfuric acid was largely composed of naphthenes and paraffins.

The oil residue that was completely soluble in sulfuric acid was distilled by Engler [43] with production of compounds of the olefin and paraffin series, and probably of the naphthene series. The decomposition began at about 200° C., and gas formation at 300° C. The lower boiling fractions contained paraffins, olefins, and naphthenes, and the higher boiling fractions olefins, naphthenes, and other hydrocarbons

[39] *Ber.*, 30 (1897), 2919-20.
[40] *Z. Ang. Chem.*, 19 (1897), 619-623.
[41] *Ber.*, 30 (1897), 2911-2914.
[42] *Ber.*, 30 (1897), 2915-19.
[43] *Ber.*, 30 (1897), 2909.

with a lower hydrogen content. The naphthenes were probably formed from the olefins by secondary reactions.

A fraction from Baku petroleum, boiling at 360° to 420° C. was heated to 450° C. in a closed wrought-iron vessel by G. Kramer and A. Spilker.[44] 500 grams yielded 50 to 100 liters of gas, 320 grams of distillate, and 50 grams of a pitchy residue. The gas contained 20.8 per cent of olefins. The balance was largely methane with small amounts of higher homologues. The liquid contained a large percentage of olefins, and also a residue of hydrocarbons not removed by concentrated or fuming sulfuric acid. The hydrocarbons of this residue were not identified, but the authors expressed the opinion that the paraffins were not present in large amount.

In an extensive investigation of the decomposition of alcohols under high pressure in the presence of catalyzers such as iron or aluminum, Ipatiev [45] came to the conclusion that in the decomposition of all organic substances under the influence of a long slow heating and of pressure, the gases given off were poorer in hydrogen and carbon monoxide the higher the pressure, and that the gas evolution ceased completely at very high pressures.

Engler [46] discusses the theory of the decomposition of hydrocarbons. By careful working under pressure, with moderate temperature, and with allowance of sufficient time, the long-chain hydrocarbons split near the middle of the molecule. But at higher temperature, and under less pressure, the rupture takes place nearer the end of the chain, with a resultant decrease in the amount of middle decomposition products, and with an increase in gaseous and high boiling products.

Engler and Halmai [47] found that paraffins, olefins, naphthenes, and a tarry residue were formed when a heavy cylinder oil from Baku petroleum was heated in an autoclave.

B. T. Brooks [48, 49] and co-workers have experimentally investigated the decomposition of petroleum under pressure. An Oklahoma reduced oil of 30° Bé. was treated in a laboratory pressure-still in such a manner that runs were made at different pressures between ordinary pressure and 400 lbs. per sq. in. The temperatures ranged from 275 to 420° C. The yield of "gasoline" (i.e., distillate to 150° C. in the subsequent laboratory examination of the products), and the "refining loss" (treatment with $\frac{1}{10}$ volume of concentrated sulfuric acid) are shown in Figure 94. The authors are of the opinion that the decrease in olefins with increase of pressure is the result of polymerization and not of hydrogenation. They showed that a sample of cracked naphtha was unaffected when heated to 196° C. under 300 lbs. per sq. in. pressure for thirty hours in the presence of hydrogen gas. The iodine number was 55.0 at the start of the experiment and 52.9 at its conclusion.

[44] *Ber.*, 33 (1900), 2265-70.
[45] *Ber.*, 37, 1904, 2982.
[46] *D. Erd.*, Vol. 1, 565 *et seq.*
[47] *Ber.*, 43, 1910, 388.
[48] *J. Fr. Inst.*, 180 (1915), 653.
[49] *J. Ind. Eng. Chem.*, 7 (1915), 180-5.

The removal of the gasoline as fast as formed was important, since in experiments in which the oil was heated in a closed vessel and later removed and distilled, only 4 per cent of gasoline was obtained. In the experiments, the results of which are given above, the gasoline was removed as it was formed.

These investigators have also recorded the composition of the gases evolved during the pressure distillation of Jennings, La., reduced oil boiling above 265° C. and of paraffin.

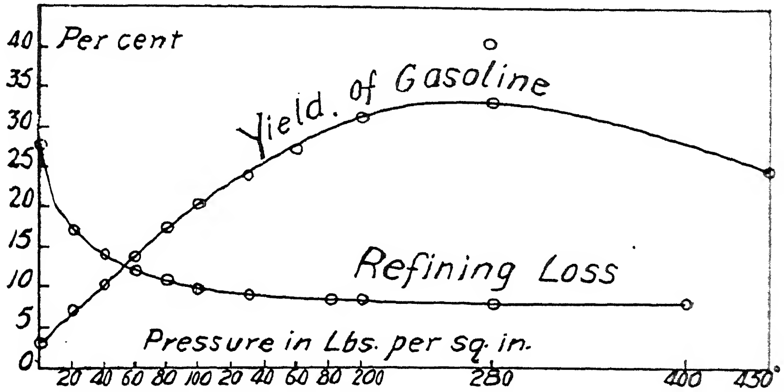


FIG. 94.—Yields and Refining Losses of Gasoline Obtained by Distilling Oklahoma Reduced Oil Under Pressure.

TABLE LV

ANALYSIS OF GASES EVOLVED DURING PRESSURE DISTILLATION OF LOUISIANA OILS, AND OF PARRAFIN

	Jennings' Reduced Crude			Paraffins		
	I	II	III	I	II	III
Temp. in Still	340° C.	415° C.	422° C.	417° C.	432° C.	437° C.
CO_2	1.2	0.5	0.0	0.0	0.0	0.0
CO	1.2	0.5	1.3	0.0	0.0	0.0
Illuminants	15.4	15.3	13.0	25.4	37.0	33.5
Hydrogen	0.0	4.0	4.4	0.3	0.9	3.0
Saturated Hydrocarbons	81.5	79.7	81.3	74.3	62.1	63.5

These samples were taken as the pressure distillations proceeded. As will be noted the temperatures increased. A higher temperature was necessary for the decomposition of the paraffin than for the reduced Jennings crude.

A further interesting observation of Brooks and his collaborators was the finding of 8 per cent benzene, toluene and xylene in the gasoline

made by the pressure distillation of a reduced Oklahoma crude oil. They stated that, other than these aromatic compounds and the olefins, the gasoline consisted of paraffin hydrocarbons.

SUMMARY.

Decomposition of an oil in a liquid-vapor system gives results that are different from those obtained when the oil is first vaporized and then thermally treated. The decomposition starts at about 200° C., but is not rapid until temperatures above 350° C. are reached. The evolution of gas starts at about 300° C. The gas is largely methane, but as the temperature rises ethylene and hydrogen are found in it in small to moderate amounts. The liquid products are olefins, paraffins, and heavy hydrocarbons of high carbon and low hydrogen content. Polymethylene compounds are probably formed, at least from those oils that originally contain cyclic compounds. The percentage of olefins is larger in the higher boiling fractions of the products than in the lower boiling portions. This is quite in contrast to the results ordinarily recorded in investigations of the nature of the products formed in the vapor-phase treatment of oils. Conclusions of this sort are none too certain, however, since they are based on analytical determinations of olefins by means of concentrated sulfuric acid. It is now well known that many of the higher olefins combine scarcely at all with sulfuric acid.

Apparently when the higher hydrocarbons in liquid form are heated the tendency is for the molecules to split near the middle of the chain. This is in contrast to the predominant reaction in the decomposition of hydrocarbon vapors, which is mainly a splitting off of low molecular weight paraffins. To what extent the difference in the reactions in the vapor state and in the liquid state is the result of physical state rather than of temperature or time of reaction, cannot now be definitely stated. I have already suggested that important difference may exist as a result of the presence of liquid surfaces, and the consequent influence of the surface energy on the nature of the reactions.

The application of pressure has the effect of diminishing the gas formation.

Secondary Thermal Reactions—Reactions of the Higher Molecular Weight Olefins.

The higher olefins are formed as primary products when the higher araffins are thermally treated. An understanding of the reactions of
long chain olefins is essential to knowledge of the course of the
of hydrocarbon decomposition. Unfortunately, this phase of
hydrocarbon reactions has received little attention, surely
s importance merits.
se of the primary reactions of the hydrocarbons, chemi-
he vapor state must be distinguished from those in the

Reactions in the Vapor State.

So far as the writer is aware no work has been published on the thermal reactions of the higher olefins in the vapor state. We are, however, not entirely at a loss, in picturing possible and even probable reactions of the heated vapors of these substances. As an aid to this process the work of a few investigators may be cited. H. E. Armstrong [50] found a gas dissolved in the compression liquids from oil-gas manufacture that formed a bromide of the composition $C_4H_6Br_4$. He believed this hydrocarbon was methylallene.

Armstrong and Miller [51] have isolated vinylethylene $CH_2=CH-CH=CH_2$, and an hydrocarbon of formula C_5H_8 that they believed after a careful investigation, was unsymmetrical dimethylallene

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} > C = C = CH_2$$

Haber [52] was convinced by a study of the combustion data on oil-gases made from hexane at temperatures of 600° C. and above, that naphthenes were present. He believed that crotonylene was formed in small amounts by the splitting of methane from amylene. He also lays emphasis on the polymerization and condensation process by which tarry substances are formed from "free unsaturated residues."

Worstall and Burwell [53] worked on oil-gas tars in an effort to determine whether or not naphthenes were present. They mentioned that the absence of naphthenes in residues from nitration or sulfonation treatment of oils is not evidence that no naphthenes are present, for the naphthenes nitrate to aromatic nitro compounds. Such compounds have been obtained by the use of dilute nitric acid.[54] From the results of distillation and specific gravity tests the authors concluded that their oil-gas tars contained no naphthenes.

In my opinion the difference between the results of Worstall and Burwell and those of Haber or Engler can be explained on the basis of the fact that the oil-gas residues examined by the former investigators were made at temperatures of 850 to 900° C., whereas Haber and Engler worked at temperatures 300 to 500° C. lower than this. The naphthenes are rapidly decomposed thermally at temperatures of 850 to 900° C.

A. Harzer [55] commented on the fact that diolefins were to be found in coal tar.

The composition of the gases formed from paraffin hydrocarbons when thermally treated is significant. The work of Engler, cited earlier in this chapter, should be recalled at this point. When pentane vapor

[50] *J. Soc. Chem. Ind.*, 3 (1884), 462-468.
[51] *J. Chem. Soc.*, 49 (1886), 80-85.
[52] *J. Gasbel*, 39 (1896), 377-82, 395-99, 435-39, 452-55, 799-805, 813-18, 830-34.
[53] *Am. Chem. J.*, 19 (1897), 815-45.
[54] *Ber.*, 25 (1892), 107-8; 28 (1895), 577-8.
[55] *Gas World*, 59 (1913), 405.

was slowly passed through a tube heated to 480° C. the gas formed was almost pure methane. No hydrogen and only 1.5 per cent of ethylene accompanied the methane. As the temperature increased the percentage of ethylene increased, as was shown by Engler in his experiments on the thermal treatment of several distillates from a paraffin-base petroleum.

The work of several other investigators is of interest in this connection. W. A. Noyes, W. M. Blinks, and A. V. H. Morey [56] made oil-gases at comparatively low temperatures in a checker-brick filled machine. The gases were analyzed for olefins by passing through bromine water, and subsequently fractionating the bromides formed. In this manner they found that of the 28.1 per cent of olefins in the gas 16.2 per cent was ethylene and 11.9 per cent propylene.

Norton and Andrews [57] passed the gases formed in the thermal treatment of pentane and hexane through bromine dissolved in carbon disulphide. The liquid bromides were found to be ethylene and propylene dibromides in almost equal amount. They also found a solid tetrabromide $C_4H_6Br_4$ that they believed to be the bromine addition compound of divinyl or crotonylene.

Burrell, Seibert and Robertson [58] have analyzed Pittsburgh coal- and water-gases by the fractional distillation of the liquefied gases. The method is exacting and tedious, but the results are accurate. Table LVI shows the proportions of the various components that make up the 3.99 per cent of illuminants in the coal gas, and the 15.9 per cent in the carbureted water-gas.

TABLE LVI

HYDROCARBON COMPONENTS OF PITTSBURGH COAL- AND WATER-GAS

Component	Coal-Gas	Carbureted Water-Gas
Ethylene	53.8	60.9
Propylene	7.7	17.4
Butylene	2.6	10.6
Propane	....	1.8
Butane	....	....
Benzene (a)	35.9	9.3

(a) Vapors having an inappreciable vapor pressure at 78° C.

The significant feature of these results is the proof of the presence of the olefins of three and four carbon atoms, and of the absence of the corresponding paraffins.

The writer [59] has decomposed a paraffin-base kerosene by passing it in vapor form through a carbon tube-furnace heated to 825° C. Even at this relatively high temperature the olefins in the gas were one-third propylene.

[56] *J. Am. Chem. Soc.*, 16 (1894), 688-97.
[57] *Am. Chem. J.*, 8 (1886), 1-9.
[58] U. S. Bur. of Min., "Tech. Ppr. No. 104."
[59] *J. Ind. Eng. Chem.*, 8 (1916), 593-601.

The observations of these several workers may be interpreted as meaning that the higher molecular weight olefins, formed in the primary decomposition of the paraffins, decompose yielding olefins of lower molecular weight. Thus amylene on scission forms ethylene and propylene.

$$CH_3CH_2CH_2CH = CH_2 \longrightarrow CH_3—CH = CH_2 + CH_2 = CH_2$$

Reactions of this type would explain the relatively high olefin content of the gases formed when paraffin hydrocarbons are decomposed at temperatures between 500 and 800° C. It might be argued that the paraffins split with formation of low molecular weight olefins and long chain paraffin, but this is contrary to the observations of experimenters whose work has already been cited.

The presence of diolefins or isomeric substituted acetylenes in the products from thermally treated hydrocarbons can be explained by assuming that a reaction takes place similar to the reaction of primary decomposition of the paraffin hydrocarbons. This may be illustrated by the following equation:

$$CH_3CH_2CH_2CH = CH_2 \longrightarrow CH_2 = CH—CH = CH_2 + CH_4$$

Tautomeric change from butadiene to crotonylene explains the presence of the latter substance.

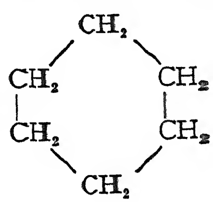
At least three other type reactions are probably among the chemical changes that take place in the vapor-phase thermal treatment of olefins. This may be illustrated by the reaction:

$$RCH_2—CH = CH_2 + RCH_2—CH = CH_2 \longrightarrow$$

$$R—CH_2—\underset{H}{\overset{H}{C}}—CH_2—\overset{R}{CH}—CH = CH_2$$

Reactions of this type are of great importance in the thermal treatment of liquid olefins, but to what extent they take place in hydrocarbon systems in the vapor state cannot be said at present.

A second type of reaction is one in which the open chain olefins forms a polymethylene. This may be illustrated by the equation:

$$CH_3CH_2CH_2CH_2CH = CH_2 \longrightarrow$$ 

Polymethylene hydrocarbons are formed from liquid olefins, but there is little conclusive evidence to prove that reactions similar to the above occur in the vapor state. The formation of the stable five and six

carbon ring compounds in this manner is not improbable. In the case of the less stable ring compounds such as cyclopropane the reverse change is known to take place with formation of propylene.

Lastly the olefins may hydrogenate. In the vapor state, except at the lowest temperatures, hydrogen is always present in some quantity, and it is possible that paraffins may be formed by hydrogenation. No experimental evidence is at hand to indicate the extent of this reaction.

Thermal Reactions of Olefins in the Liquid State.

This subject like that of the reactions of the olefins in the vapor state is in need of further study. The mechanism of the reactions is not understood, though the general nature of the products obtained by heating butylenes, amylenes, and hexylenes under pressure is known. The most important work in this field is briefly reviewed in the following paragraphs.

One of the earliest investigations of the effect of heating the liquid olefins was that of Engler and Eberle.[60] A hexylene sym-methylethylene was heated for 14 days at 360 to 365° C. in a sealed tube. The hexylene boiled at 67 to 68° C. and had a specific gravity of 0.6870. The product boiled between 67 and 240° C. (35 per cent from 67 to 85° C., 58 per cent 86 to 240° C., 7 per cent residue). The absorption of bromine by the products was less than the absorption by the hexylene, and least by the higher boiling fractions. The lower boiling paraffins and the naphthenes, particularly n-hexane and dodecanaphthene were formed along with a heavy residue. The investigators were of the opinion that the heavy residues were not a direct polymerization product of the olefins since they were poorer in hydrogen than an hydrocarbon of empirical formula C_nH_{2n}. Apparently the olefins polymerize to compounds that subsequently decompose to hydrocarbons of higher and of lower hydrogen content. When olefins or heavy-oil residues are heated under pressure the products are paraffins, naphthenes, and heavy residues. The paraffins compose the larger part of the lower boiling fractions. As the boiling point of the fractions increases the proportion of naphthene hydrocarbons increases.

Engler and Routala[61] showed that little change took place when amylene was heated a few hours at 70° C. in a sealed tube. On the other hand, heating for eleven days at 230° C. raised the specific gravity from 0.6647 to 0.6725, and halved the bromine absorption. The product was fluorescent and of greenish-yellow color. Heating amylene 12 days at 330° C. caused an even more marked change. The specific gravity increased from 0.6647 to 0.7505. The formation of polymethylenes is shown by the high specific gravity. Heating at 350° C. raised the specific gravity to 0.7801. Separation of carbon was noted at this temperature.

In another experiment 350 grams of commercial amylene was heated

[60] *Petroleum*, 2 (1907), 915; *Das Erdöl*, Vol. 1, 332-337.
[61] *Ber.*, 42 (1909), 4620-31.

32 days at 320 to 325° C. Ten liters of gas was formed, composed of 10 per cent H_2, 1.5 per cent olefins, and 91.1 per cent saturated hydrocarbons. The liquid product had a bluish-green fluorescence, and a terpene-like odor. Somewhat over one-third boiled from 29 to 145° C., about one-third from 145-189° C., and slightly less than one-third from 189 to 300° C. The specific gravity of the various fractions was always higher than that of the olefins or paraffins of the same boiling point. The higher boiling fractions contained large amounts of olefins as shown by the extensive oxidation as the oils stood in contact with the air. The olefins were removed from the products by the use of fuming sulfuric acid followed by washing with caustic soda solution. The residual hydrocarbon mixture was fractionated over sodium. The various fractions were examined, and it was shown that pentanes, hexanes, heptanes, cyclohexane, methyl cyclopentane, heptanaphthene, octane, octonaphthene, nononaphthene, decanaphthene, hendecanaphthene, dodecanaphthene, tetradecanaphthene, pentadecanaphthene, and higher naphthenes were present. In the highest boiling fractions and residue hydrocarbons poorer in hydrogen than the naphthenes were present.

The polymerization of the olefins has been studied by Ipatiew.[62] Isobutylene was heated to 380 to 390° C. in a closed tube. From 500 grams of isobutylene a liquid product was obtained that distilled as shown below:

° C.	Grams
23-100	70
100-150	105
150-190	55
190-215	58
215-260	82
260-280	55
over 280	60

The composition of all these fractions indicated that the lower boiling fraction contained paraffins as well as olefins, and that the higher boiling fractions were composed of olefins, polymethylenes and smaller amounts of paraffins. The presence of the olefins in the lower boiling fractions indicated that isobutylene polymerizes to di- and tri-isobutylene.

$$\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\!\!>C=C<\!\!\begin{matrix} H \\ \\ H \end{matrix} + \begin{matrix} H \\ \\ H \end{matrix}\!\!>C=C<\!\!\begin{matrix} CH_3 \\ \\ CH_3 \end{matrix} \longrightarrow \begin{matrix} CH_3 \\ \\ CH_3 \end{matrix}\!\!>C=\overset{\displaystyle H}{C}-C\!\begin{matrix} \diagup CH_3 \\ -CH_3 \\ \diagdown CH_3 \end{matrix}$$

In this manner tri- and tetra-polymeric products are formed from this and from other olefins.

[62] *Ber.*, 44 (1911), 2978.

Summary—Reactions of the Olefins in the Liquid State.

From the above investigations it is evident that the butylenes, amylenes and hexylenes, when heated under pressure to temperatures between 200 and 400° C., form di-, tri-, tetra-, and probably higher polymers. The further course of the reactions involved is not clear, but the products are paraffins, polymethylenes, higher olefins, and hydrocarbons of lower hydrogen content than the olefins.

Thermal Reactions of the Simpler Hydrocarbons.

The thermal reactions of the simpler hydrocarbons methane, ethane, propane, butane, ethylene, propylene, butylene, acetylene, and propane are of small moment to the manufacturer of motor fuels, but of the greatest importance to the user of motor fuel. The real importance in this latter connection has not been appreciated, and is not now appreciated. I am of the opinion that fuller knowledge of the thermal reactions of these simple hydrocarbons that are always formed in extensive decompositions of the higher hydrocarbons will aid materially in explaining the complex phenomena of combustion within the cylinders of an explosion motor. For this reason a brief résumé of our present knowledge of this subject is included here, and references are given in order that the reader may further investigate the literature of the subject.

Reactions of Methane.

Methane is the most stable of all hydrocarbons at temperatures up to 1200° C. and is consequently found in all gaseous mixtures made by the decomposition of hydrocarbons. At higher temperatures (1800 to 2500° C.) acetylene is formed from carbon and hydrogen, as shown by Pring and Hutton.[63]

The methane-carbon-hydrogen equilibrium has been studied by a number of investigators, among whom may be mentioned Mayer and Altmayer,[64] Pring and Fairlie,[65] and Coward and Wilson.[66]

Coward and Wilson give the following as the composition of equilibrium mixtures of methane and hydrogen in contact with amorphous carbon at atmospheric pressure.

	1100° C. %	1000° C. %	850° C. %
Methane	0.6	1.1	2.5
Hydrogen	99.4	98.9	97.5

At lower temperatures the reaction mixture did not come to equilibrium within any reasonable length of time.

[63] *J. Chem. Soc.*, 89 (1906), 1591-1601.
[64] *Ber.*, 40 (1907), 2134-2144.
[65] *Rep. 8th Int. Cong. App. Chem.*, 21, 65.
[66] *J. Chem. Soc.*, 115 (1919), 1380-7.

Pring and Fairlie have shown that at 1300° C. ethylene begins to be formed and that at 1650° C. the formation of acetylene starts. At those temperatures at which ethylene and acetylene are formed no exact determination of the methane equilibrium is possible since this hydrocarbon is formed by the decomposition of ethylene or acetylene. The amounts of methane in equilibrium at 1200 and 1500° C. are given as 0.20 per cent and 0.07 per cent respectively.

The investigations of the methane equilibrium are of interest, but it is perhaps more important to know the rate of decomposition of methane at various temperatures.

Bone and Coward found that the decomposition of methane was inappreciable at 700° C. In an experiment at 785° they found that 91.6 per cent of the methane used was unchanged at the end of one hour. The results of other experiments are shown in Table LVII.

TABLE LVII

PRODUCTS OF THERMAL DECOMPOSITION OF METHANE AT SEVERAL TEMPERATURES

Temperature (° C.)	Duration of Heating in Minutes	Percentage Composition of the Gaseous Products			
		Acetylene	Unsaturated Hydrocarbons	Methane	Hydrogen
985	1	0.5	0.3	90.4	8.8
985	5	0.5	0.5	75.4	23.6
985	30	nil	0.35	62.85	36.8
1000	15	nil	1.3	65.25	33.3
1015	60	nil	nil	48.2	51.2
1150	1	0.5	nil	44.6	54.9
1150	5	nil	nil	27.25	72.25
1160	60	nil	nil	22.3	77.7
1150-1160 ...	180	nil	nil	9.15	90.85

These authors came to the conclusion that the decomposition of methane is largely if not entirely a surface action. When the reaction vessel was filled with fragments of quicklime only 1.9 per cent of methane remained after 25 minutes of heating at 1030° C., and only 0.7 per cent after heating for one hour. The carbon formed by the decomposition of methane is of a peculiarly hard and lustrous variety, almost metallic in appearance, and quite different from the soft dull variety formed from acetylene or ethylene.

Hollings and Cobb [67] passed a mixture of equal parts of hydrogen and methane through an electrically heated tube. At 800° C. it was found that only 2 per cent of the methane was decomposed in one minute. At 1100° C., 65 per cent of the methane was decomposed in 47 seconds.

Whitaker and Alexander [68] showed that methane was the last gas

[67] *Gas World*, 60 (1914), 879-884.
[68] *J. Ind. Eng. Chem.*, 7 (1915), 484-495.

in a complex hydrocarbon mixture to be decomposed at temperatures between 1400° C. and 1600° C.

From the foregoing investigations it is evident that the chief thermal reaction of methane is its dissociation into carbon and hydrogen.

$$CH_4 \rightleftarrows C + 2H_2$$

Other reactions such as $CH_4 + CH_4 \longrightarrow CH_3 - CH_3 + H_2$ are possible, but are of minor importance.

OTHER REFERENCES ON METHANE AND ITS THERMAL REACTIONS

Lewes, *J. Chem. Soc.*, 61 (1892), 322-338. *Proc. Roy. Soc.*, 55 (1894), 90; 57 (1895), 394.
Bone and Jordan, *J. Chem. Soc.*, 71 (1897), 41-46.
Holgate, T., *J. Gas Lighting*, 106 (1909), 25-28, 84-86.
Ipatiew, W., *J. Prakt. Chem.*, 87 (1913), 479-487.
Simmensbach, *St. u. Eis.*, 33 (1913), 239-45.

For a very complete bibliography and résumé of the properties of methane see article by W. Masiloff and G. Egloff.[69]

Reactions of Ethane.

The thermal decomposition of ethane has been the object of few investigations. The work of Bone and Coward [70] is the only work of importance. In one experiment ethane was circulated through a tube heated to 675° C., and samples were withdrawn for analysis at intervals. The results are shown in Table LVIII.

TABLE LVIII

Products of Thermal Decomposition of Ethane at 675° C.

Time in Hours	$\frac{P_2}{P_1}$, i.e., Ratio of Pressure in Apparatus to Initial Pressure (248 mm.)	Per Cents				
		Acetylene	Ethylene	Ethane	Methane	Hydrogen
½	1.47	4.1	24.7	34.7	8.4	28.1
1½	1.70	5.1	24.1	9.8	19.9	41.1
3.0	1.80	2.8	16.4	7.3	32.9	40.6
6.0	1.87	1.9	0.7	2.0	54.5	40.9

: end of the experiment soft, flaky carbon was found in the n tube. A small amount of naphthalene was found, but apparno benzene.

idently the reactions involved are,

. *Phys. Chem.*, 22 (1918), 529-575.
. *Chem. Soc.*, 93 (1908), 1197-1225.

$$C_2H_6 \rightleftarrows C_2H_4 + H_2$$
$$C_2H_4 \rightleftarrows C_2H_2 + H_2$$
$$C_2H_2 \rightleftarrows 2C + H_2$$
$$C_2H_6 + H_2 \rightleftarrows 2CH_4$$

The last reaction is not suggested by Bone and Coward. They postulate hydrogenation of unsaturated "residues," such as $=CH_2$ and $\equiv CH$. This seems unnecessary, for the reaction last written above is one that would be expected if reaction possibilities are considered from the standpoint of molecular kinetics. It is of interest to note the results of experiments in which mixtures composed of $C_2H_6:3N_2$ and $C_2H_6:3H_2$ were heated for one hour to 800° C. in a closed tube. The resultant gaseous mixture contained 41.25 per cent of methane when the ethane-hydrogen mixture was heated as compared to 18.15 per cent when the ethane-nitrogen mixture was heated.

At 800° C. ethane decomposes rapidly. In one minute's heating the gas had the composition acetylene 1.9 per cent, ethylene 11.2 per cent, ethane 17.9 per cent, methane 31.3 per cent and hydrogen 37.7 per cent. After one hour's heating only methane (63.75 per cent) and hydrogen (36.25 per cent) remained.

One minute's heating of ethane at 1000° C. resulted in an extensive decomposition. The composition of the resulting gas was acetylene 2.5 per cent, ethylene 6.9 per cent, ethane 5.5 per cent, methane 32.6 per cent, and hydrogen 52.5 per cent. The longer the time of heating the more extensive the decomposition.

At temperatures between 1140 and 1185° C. the decomposition of ethane was very rapid. The gas scarcely survived a single rapid passage through the hot tube. The product after five minutes' heating was composed of methane 27.0 per cent and hydrogen 73.0 per cent.

The work of Hollings and Cobb [71] adds nothing to the results of Bone and Coward, though it is confirmatory and worthy of mention.

Reactions of Propane and Butane.

The thermal reactions of propane and butane have not been thoroughly studied, and it is impossible to discuss the subject in detail.

Zanetti,[72] and Zanetti and Leslie,[73] have investigated the reactions of the propane-butane, and the ethane-propane fractions from natural-gas condensate. These researches were made largely for the purpose of studying the formation of aromatic hydrocarbons from the simpler paraffins. Gases consisting of ethylene, propylene, and higher olefins, methane and unchanged ethane, propane, and butane, hydrogen, and aromatic hydrocarbons were formed. The liquid products consisted of benzene, toluene, naphthalene and other aromatic hydrocarbons.

J. G. Davidson [74] working in Professor Zanetti's laboratory studied

[71] *Gas World*, 60 (1914), 879-884.
[72] *J. Ind. Eng. Chem.*, 8 (1916), 674-79.
[73] *J. Ind. Eng. Chem.*, 8 (1916), 777-79.
[74] *J. Ind. Eng. Chem.*, 10 (1918), 901-910.

the decomposition of the ethane-propane fraction of natural condensates with still greater care. The reactions of this gas mixture were investigated between the temperatures 550° C. and 850° C., and at pressures of 0, 25, 50, 75, and 100 lbs. gage. Ethylene, less propylene and butylene, and a large amount of butadiene were the olefinic products. The other products were methane, hydrogen, and aromatic hydrocarbons.

Apparently therefore, the reactions of these lower molecular weight paraffins are not unlike those of the higher paraffins:

$$CH_3CH_2CH_3 \longrightarrow CH_2 = CH_2 + CH_4$$
$$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH = CH_2 + CH_4$$

Dissociation of ethane or ethylene and decomposition of methane account for the presence of hydrogen. The butadiene was formed by the polymerization of ethylene, and the aromatic hydrocarbons by the polymerization of the butadiene, or possibly of the mono-olefins, to hydro-aromatic compounds that were subsequently dehydrogenated.

Reactions of Ethylene.

Ethylene, next to methane, is the most important of the gaseous hydrocarbons. It is found in large quantity whenever the higher paraffins or the polymethylenes are thermally decomposed. The reactions of ethylene are therefore of importance.

Day,[75] in summing up the work of Fourcroy, De-Wilde, Buff, Hoffman, Berthelot, Marchand, Grove, and Magnus, says: "It seems clear that at the highest temperatures ethylene separates directly into its elements. Below this point marsh gas and carbon are obtained ($C_2H_4 \longrightarrow CH_4 + C$), then marsh gas and several liquid products, among them benzene, styrene, etc., under certain conditions." Day circulated ethylene through a glass tube heated to various temperatures for different lengths of time. No change in volume was observed in 14 hours' heating at 300° C. At 344° C., a contraction of one-twentieth of the original volume took place in 24 hours, and as no methane or hydrogen was found in the gas Day concluded that condensation had taken place. At 400° C., 132 cc. of ethylene contracted to 63 cc. in 171 hours. No hydrogen was present in the final gas, which was a mixture of 22.4 c.. methane, 24.8 cc. ethane, and 15.6 cc. ethylene or other olefins.

Norton and Noyes[76] passed ethylene slowly through a glass tube heated to a red heat for 60 cm. of its length. The products passed out through a series of U-tubes immersed in a freezing mixture, then through ammoniacal cuprous chloride, through bromine, and finally to a gasometer. Carbon was deposited in the tube. From the liquid condensed in the freezing mixture benzene and naphthalene were isolated. Only traces of acetylene were in the gases, and the authors

[75] *Am. Chem. J.*, 8 (1886), 153-167.
[76] *Am. Chem. J.*, 8 (1886), 153-167.

concluded that if acetylene were formed it must have been decomposed in the tube. The liquid bromides collected consisted chiefly of ethylene dibromide, but also contained some methylene dibromide, propylene dibromide, and butylene dibromide. The solid bromides had the composition of $C_4H_6Br_4$, and Norton and Noyes believed that this could be explained by the reaction $2C_2H_4 \longrightarrow C_4H_6 + H_2$. The gases collected consisted of methane and ethane.

The most valuable work on the thermal reactions of ethylene is that of Bone and Coward.[77] They circulated the gas for a period of 2½ hours through a tube heated to 570 to 580° C. Acetylene, ethane, methane, hydrogen, and aromatic hydrocarbons were produced in quantity. The carbon separated was negligible. Methane accumulated rapidly and continuously, hydrogen accumulated during the first 60 minutes and then decreased slightly, and acetylene varied somewhat irregularly from 12 per cent of the gases after 2 minutes' heating to 6 per cent of the gases at the end of the experiment. The weight of carbon in the gases diminished progressively until at the end of the experiment it was only one-half that contained at the beginning.

The authors believe that acetylene is a primary dissociation product of ethylene.

$$C_2H_4 \rightleftarrows C_2H_2 + H_2$$

They contend that their experimental work proves that Lewes was in error in his belief that the main reaction involved in the decomposition of ethylene was

$$3C_2H_4 \longrightarrow 2C_2H_2 + 2CH_4$$

for were this the reaction, the rate of accumulation of methane would be ⅔ the rate of disappearance of ethylene, whereas, in fact, it is only ⅓. Methane is stable at the temperatures used in this experiment.

The above experiment also proves that the reaction

$$C_2H_4 \longrightarrow C + CH_4$$

is of small importance at 570 to 580° C.

The results of the treatment of ethylene at 800° C. are shown in Table LIX. In this instance the gas was not circulated but was simply heated in the reaction vessel. A larger separation of carbon and a smaller formation of aromatic hydrocarbons occurred at 800° C. than at 580° C. Acetylene and ethane were still produced, but to a lesser extent than at the lower temperature. Methane was found in much larger quantity, the ratio of $CH_4 . H_2$ never falling below 3.0 as compared to a ratio of less than 1.0 at 580° C. The authors explain this on the basis of the assumption that unsaturated residues such as $=CH_2$ or $\equiv CH$ are hydrogenated.

It was shown that when mixtures of ethylene with hydrogen and with nitrogen in the proportion $C_2H_4 + 3H_2$ and $C_2H_4 + 3N_2$ were

[77] *J. Chem. Soc.*, 93 (1908), 1197-1225.

TABLE LIX

PRODUCTS OF THERMAL TREATMENT OF ETHYLENE AT 800° C.

Percentage Composition of the Products	Time of Heating in Minutes			
	1	5	15	30
C_2H_2	3.00	23.9	3.85	nil
C_2H_4	57.25	1.4	9.65	0.9
C_2H_6	3.25	5.0	1.3	nil
CH_4	29.4	53.4	64.45	67.7
H_2	7.1	17.0	20.75	31.4

thermally treated the percentage of methane in the gaseous products was 43.5 in the case of the hydrogen mixture and only 13.8 in the case of the nitrogen mixture.

When ethylene was heated at 950° C. 90 per cent decomposed within one minute, and scarcely any survived a 15-minute treatment. Only small amounts of aromatic hydrocarbons were produced, but large quantities of carbon separated. The gases were largely methane and hydrogen. At 1180° C. the results were similar. Ethylene was rapidly and completely decomposed into carbon, methane, and hydrogen.

The polymerization of ethylene was studied by W. Ipatiew.[78] The gas was compressed to 70 atmospheres in an iron tube. Polymerization started at 325° C., was moderately rapid at 350°, and very rapid at 380 to 400° C. The residual examined after a typical experiment had the composition C_nH_{2n} 52.8 per cent, H_2 4.2 per cent, C_nH_{2n-2} 43 per cent. Forty to fifty grams of liquid products were produced from an original quantity of 30 liters of ethylene. The liquid products were shown to be composed of olefins, paraffins, and large amounts of polymethylenes. These products boiled from 24° C. to well over 280° C. Ipatiew comments on the fact that the polymerization did not occur if pressure was not applied. When ethylene was slowly led through an iron tube at 600° C. little change occurred. Ipatiew expressed the opinion that ethylene polymerized to polymethylenes just as acetylene polymerized to benzene.

H. Hollings and J. W. Cobb[79] passed a gas mixture containing 10.6 per cent ethylene, 47.7 per cent methane, and 41.7 per cent hydrogen through a tube heated to 800° C. The gases exiting from the tube after 45 seconds heating contained 4.5 per cent ethylene, 54.4 per cent methane, 40.3 per cent hydrogen and 0.8 per cent acetylene. No benzene or ethane were found. Methane and acetylene appeared to be the chief products. Apparently the reactions taking place were: $C_2H_2 \longrightarrow CH_4 + C$ and $C_2H_4 \longrightarrow C_2H_2 + H_2$. The first of these reactions was much the most important. A contraction in volume took place which the authors believed resulted from the formation of liquid prod-

[78] *Ber.*, 44 (1911), 2978-87.
[79] *Gas World*, 60 (1914), 879-84.

ucts. At 1100° C. the ethylene was decomposed completely in 35 seconds' heating.

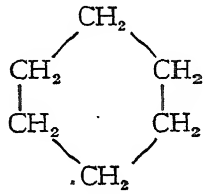
While it must be admitted that the work of the above mentioned investigators has not entirely clarified the course of the reactions involved when ethylene is heated at various temperatures, it can at least be said that we are possessed of fair indications as to the nature of these reactions.

The most important reaction at temperatures up to 700° C. is the dissociation into acetylene and hydrogen.

$$H_2C = CH_2 \rightleftarrows HC \equiv CH + H_2$$

The polymerization of ethylene to higher olefins or polymethylenes is also indicated.

$$H_2C = CH_2 + H_2C = CH_2 \longrightarrow H_3C - CH_2 - CH = CH_2$$

$$3C_2H_4 \longrightarrow$$ 

The velocity of these reactions may be slow except when pressure is applied, but the presence in reaction products of the polymethylenes, and also of a variety of open chains hydrocarbons of more than two carbon atoms, shows that changes of this sort occur to some extent.

The presence of hydrogen in the gaseous products formed at temperatures under 700° C. may be explained by the dissociation of ethylene into acetylene and hydrogen, and also by the fact that acetylene decomposes into carbon and hydrogen.

In the presence of hydrogen reactions with this gas take place. Thus ethylene is hydrogenated to ethane

$$C_2H_4 + H_2 \rightleftarrows C_2H_6$$

Ethane in all probability also reacts with hydrogen.

$$C_2H_6 + H_2 \rightleftarrows 2CH_4$$

The latter reaction explains in part at least the presence of methane in the gaseous products at temperatures under 700° C.

It seems unnecessary to postulate the existence of free radicals such as $= CH_2$ or $\equiv CH$, as has been done by Bone and Coward. The reactions can be explained equally well on the basis of the ordinary conceptions of the molecular hypothesis.

At temperatures above 700° C. the decomposition of ethylene into carbon and methane is the reaction of importance.

$$C_2H_4 \longrightarrow C + CH_4$$

This probably explains the more extensive separation of carbon and the more rapid formation of methane.

At temperatures above 1200° C., the decomposition of ethylene is very rapid and complete. The products are carbon, hydrogen, and methane.

OTHER REFERENCES ON THERMAL REACTION OF ETHYLENE

LEWES, V. B., *J. Chem. Soc.*, 61 (1892), 322-38. *J. Soc. Chem. Ind.*, 11 (1892), 584-90. *Proc. Roy. Soc.*, Lon., 55 (1894), 90. *Trans. Inc. Inst. Gas. Eng.*, 10 (1900), 111-133.

LOSANITCH, S., and JOVITCHITCH, M. Z., *Ber.*, 30 (1897), 135-9. de Montmollin. *Bull. Soc. Chim.*, 19 (1916), 242-7. *Chem. Abs.*, 10 (1916), 2871.

For a complete review and bibliography of the properties and reactions of ethylene see the article by Wm. Malisoff and G. Egloff.[80]

Reaction of Acetylene.

Berthelot advanced the theory that acetylene played a fundamental rôle in the chemical rearrangement of hydrocarbon systems. He believed it to be the stopping point between decomposition and synthesis. Berthelot's conceptions have been disproved by the work of many investigators, and acetylene assumes a place of secondary importance in the general scheme of the thermal reactions of hydrocarbons.

The presence of acetylene in hydrocarbon gases formed by decomposing higher hydrocarbons has been noted by several investigators among whom may be mentioned V. B. Lewes,[81] Haber and Oechelhauser,[82] Worstall and Burwell,[83] and Noyes, Blinks, and Morey,[84] Bone and Coward [85] showed that at 500° C. the principal change undergone by acetylene was condensation, with decomposition into its elements second in importance, and hydrogenation to ethylene, ethane, and methane least important. At 600° C. the relationship was found to be much the same. At 800° C. the gas "flashed," and the temperature locally was much higher than 800° C. The most important feature of the results at this temperature was the higher proportion of methane in the resultant gases. This could be accounted for, according to Bone and Coward, by assuming the hydrogenation of $\equiv$CH residues formed momentarily by the breaking of a triple bond. They strengthened this argument by heating acetylene in nitrogen and in hydrogen, in the ratio of $C_2H_2 + 3N_2$, and $C_2H_2 + 3H_2$, when it was found that five times as much methane was formed when the gas was mixed with hydrogen as when the change took place in nitrogen. Condensation occurred at 800° C., but far less extensively than at lower temperatures. At

[80] *J. Phys. Chem.*, 23 (1919), 65-138.
[81] *J. Soc. Chem. Ind.*, 11 (1892), 584-90.
[82] *J. Gasbel*, 39 (1896), 377-82, 385-99, 435-39, 452-55, 799-805, 813-18, 830-34.
Chem. J., 19 (1897), 815-845.
m. Chem. Soc., 16 (1894), 688-97.
m. Soc., 93 (1908), 1197-1225.

1100° C. condensation was still less important, decomposition into the elements being the chief change. The most favorable temperatures for the condensation of acetylene lie between 600 and 700° C.

A number of other investigators have studied the polymerization of acetylene. Among these may be mentioned Berthelot,[86] Lewes,[87] Jacobson,[88] Haber, Sabatier and Senderens,[89] and Anschütz.[90] The most complete work is that of Meyer and his associates.[91] A complete list of the hydrocarbons identified by Meyer as condensation products of acetylene includes hexylene, benzene, toluene, o-, m-, and p-xylene, styrene, pseudocumene, mesitylene, indene, hydrindene, naphthalene, hydronaphthalene, α and β methyl-naphthalene, 1-4, dimethyl-naphthalene, diphenyl, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthrene, pyrene, and chrysene.

The reactions of acetylene may be summarized by saying that up to 700° C. acetylene polymerizes fairly rapidly to benzene and a large number of other aromatic compounds. Decomposition into carbon and hydrogen is of secondary importance at these temperatures, and hydrogenation to ethylene, ethane, and methane is least important. At slightly higher temperatures the condensation reactions are not so rapid as the decomposition into carbon and hydrogen, or the reaction of hydrogen with acetylene. At temperatures of 1100° C. and above the decomposition into carbon and hydrogen is the all important reaction.

Reactions of Diolefins and Acetylenes.

Investigations of the thermal reactions of the diolefins and higher acetylenes have been very few. Standinger, Endle, and Harold[92] investigated the thermal reactions of the butadiene hydrocarbons. The quartz reaction tube used was 1.5 meters long and 1.5 centimeters in diameter. Isoprene vapors were passed through the tube at the rate of 19 grams per hour and at a temperature of 750° C. The products from 349 grams of isoprene were 124.7 grams of gas, 196.0 grams of tar, and 15.8 grams of "coal." The gas contained 13.6 per cent unsaturated hydrocarbons (mostly ethylene), 58 to 66.3 per cent methane, and 23.5 to 19.9 per cent hydrogen. The tar consisted of aromatic hydrocarbons.

At 400 to 500° C. the isoprene was partly unchanged, and partly polymerized to unsaturated hydrocarbons. Some terpene-like substances were formed. At 600 to 700° C. an almost complete transformation to a mixture of olefins polymers was observed, and above 800° C. aromatic hydrocarbons were formed almost exclusively.

Reduction of the pressure diminished the rate of polymerization.

[86] *Ann. Chim. Phys.*, 9, iv, 445, 469.
[87] *Trans. Inc. Inst. Gas Eng.*, 10 (1900), 111-113.
[88] *Ber.*, 10 (1877), 855.
[89] *C. r.*, 131, iv (1900), 267-70.
[90] *Ber.*, 11 (1878), 1215.
[91] *Ber.*, 45 (1912), 1609-33; 46 (1913), 3183-99; 47 (1914), 2765-74; 50 (1917), 422-41; 51 (1918), 1571-87.
[92] *Ber.*, 46 (1911). 2466-77.

Isoprene at 15 mm. pressure could be distilled several times over a platinum spiral heated to bright redness without notable change.

1-3 butadiene, and Δ1-3, 2-3 dimethyl butadiene, at 800° C. yielded aromatic hydrocarbons.

The investigators believed the formation of aromatic hydrocarbons to be the result of the formation, first, of hydroaromatic polymers, followed by additional polymerization and condensation with the diolefins to form products of high molecular weight. These terpenes or polyterpenes then decomposed into aromatic substances.

S. V. Lebedev and B. K. Merezhkovski [93] have written at length on the polymerization of the olefin hydrocarbons. Five types of polymerization are considered, representing the reactions taking place when compounds of the types of styrolene, stilbene, acetylene, allene, and divinyl polymerize. Polymers produced from cyclic monomers readily dissociate. Compounds of conjugated double-bonded structure polymerize most readily. The nature of the products in any case depends on the temperature, the nature of catalysts used, and the light. Symmetrical diethylenes yield only one dimer whereas unsymmetrical diolefins give more than one. Unlike isomerization, polymerization is not a reversible reaction in many cases. Usually the reactions resulting in the formation of dimers and polymers are concurrent and not consecutive. The constitution of the complex polymers is unknown in most cases.

The allene derivatives polymerize much more readily than the derivatives of divinyl. A continuous series of products from dimers to hexamers and above are formed, whereas in the case of the divinyl derivatives the polymerization products between dimers and high dipolymers are not formed. The dimers from allene compounds are cyclic divinyl derivatives, and the high polymers are cyclobutane derivatives. In the polymerization of the allenes the union takes place at the central carbon atom. Owing to the ready change of allene into divinyl derivatives the polymerization products of the allenes frequently contain substances obtainable from the divinyls.

The following conclusions were drawn with reference to the velocity of polymerization (v). The displacement of a substituting group from an end to a middle carbon atom in the case of a divinyl group increases (v). The reverse decreases (v). Formation of a cyclic compound from an open-chain conjugated system increases (v). Formation of a cyclic compound from an open-chain conjugated system increases (v). In homologous series (v) increases with an increase in the molecular weight of the substituting group, when the latter is at an end carbon atom, and decreases when it is at one of the middle carbon atoms. In the allene series (v) is independent of the position of the substituting groups, but increases with increase in the molecular weight of the substituting groups.

The article presents a mass of detailed information regarding the polymerization products obtainable from a number of hydrocarbons.

[93] *J. Russ. Phys. Chem. Soc.*, 45 (1913), 1249-1388.

In a further article Lebedev [94] states that upon oxidation the polymerization products of the allenes yield readily identifiable derivatives of glutaric acid. They are also optically active, whereas the dimers from the other diolefins are optically inactive.

B. K. Merezhkovski [95] studied the polymerization of tetramethyl allene. Much detailed information is presented.

L. M. Kucherov [96] studied the isomeric transformation of the diethylene hydrocarbons.

The Formation and Thermal Reactions of Aromatic Hydrocarbons.

The formation of aromatic hydrocarbons and the reactions of these hydrocarbons are subjects of possible importance to the producer and user of motor fuels. The quantity of benzene, toluene, the xylenes and higher homologues used as motor fuel is now, and for a long time will be limited to a few per cent of the total motor fuel consumption of the country. But it may be that in the processes of thermal reaction within the cylinders of an engine aromatic hydrocarbons may be formed and then burned. Should this be demonstrated the whole subject matter relative to these hydrocarbons would be of more importance.

Aromatic hydrocarbons are formed from other hydrocarbons in several ways. The condensation of acetylene to benzene, or of the higher acetylenes to benzene homologues, has been thoroughly demonstrated. Yet it is improbable that aromatic hydrocarbons are formed in this way when paraffin or polymethylene hydrocarbons are thermally treated. Davidson [97] demonstrated that when acetylene, even in so small a proportion as 1.17 per cent by volume, was mixed with the light hydrocarbons of natural-gas condensate, and the mixture passed through a heated tube at temperatures from 550 to 950° C. acetylene could always be detected in the effluent gas mixture. Yet acetylene has often been reported as absent from the gases formed in the thermal decomposition of paraffin or polymethylene hydrocarbons. On the other hand the formation of benzene and aromatic substances by the dehydrogenation of the naphthenes is a probable reaction.[98, 99, 100] The naphthenes may be present in the raw material that is being processed, or these hydrocarbons may be synthesized by the polymerization of olefins. This subject has already been discussed.

Lastly, B. T. Brooks and R. F. Bacon [101] believe that the aromatic hydrocarbons are in part formed through the decomposition of compounds containing the phenyl or other aromatic radical. They synthesized phenyl paraffins, and showed that these compounds when

[94] *J. Russ. Phys. Chem. Soc.*, 45 (1913), 1390-1.
[95] *J. Russ. Phys. Chem. Soc.*, 45 (1913), 1940-74.
[96] *J. Russ. Phys. Chem. Soc.*, 45 (1913), 1634-54.
[97] *J. Ind. Eng. Chem.*, 10 (1918), 901-10.
[98] *Ber.*, 44 (1911), 3121-25; 45 (1912), 3679-81.
[99] *J. Chem. Soc.*, 107 (1915), 1582-87.
[100] *Ber.*, 44 (1911), 2978, 2987. *J. Soc. Chem. Ind.*, 36 (1917), 3.
[101] *J. Ind. Eng. Chem.*, 7 (1915), 180.

decomposed yielded benzene. However, Ogloblin [102] has shown that the naphthenes decompose readily at 525° C. and less rapidly at lower temperatures. Hence, though it is entirely possible that Brooks and his collaborators are correct in their contentions, the formation of aromatic hydrocarbons in this manner is yet open to confirmation.

The reactions of the aromatic hydrocarbons themselves have been studied by a number of workers. The investigations of Rittman, Byron, and Egloff,[103] Rittman and Egloff,[104] Dufton and Cobb,[105] and Zanetti and Egloff [106] are of particular interest. Rittman and his coworkers studied the reactions of benzene, xylenes, toluene, naphthalene, and anthracene under the influence of various temperatures and pressures. From cymene it was found possible to produce all the other hydrocarbons. Xylene gave toluene, benzene, naphthalene, and anthracene, but no cymene. From toluene, the hydrocarbons benzene, anthracene, and naphthalene could be made. Benzene yielded only naphthalene, and anthracene; and naphthalene formed anthracene but none of the others. Diphenyl, methylnaphthalene and methylanthracene, and phenanthrene were formed in smaller amounts.

Zanetti and Egloff studied the decomposition of benzene between the temperatures 500 and 800° C. The chief products were diphenyl, diphenyl benzenes, carbon, and gas. The formation of diphenyl began at 500° C. The gas consisted of hydrogen saturated with benzene vapor. No acetylene was present. No naphthalene was found in the decomposition products. This is at variance with the results of Rittman, Byron, and Egloff. The formation of diphenyl was not favored by any catalyst, though the decomposition of benzene into carbon and hydrogen was more rapid in the presence of iron or nickel, and, at temperatures above 750° C. in the presence of copper. The formation of diphenyl was most rapid at 750° C.

Dufton and Cobb's results are also at variance with those of Rittman and his coworkers, but in general agreement with those of Zanetti and Egloff. They found that at temperatures between 500 and 900° C. the first product formed from benzene was diphenyl. Also compounds such as diphenyl benzene were formed. Toluene yielded ditolyl, and also stilbene, naphthalene, anthracene and soft pitches. The presence of hydrogen or of inert mixtures had a marked effect on the nature and extent of the reactions. This will be taken up under the discussion of the effect of atmospheres of hydrogen.

Several investigators have shown that diphenyl is formed from -nzene [107] at temperatures of 500 to 1000° C. The optimum temrature is apparently about 750° C.

[102] *Z. Ang. Chem.*, 18 (1905), 540.
[103] *J. Ind. Eng. Chem.*, 7 (1915), 1019-24.
[104] *Met. Chem. Eng.*, 14 (1916), 15-18.
150 (1920), 588-91.
Eng. Chem., 9 (1917), 350-56.
., *Ber.*, 9 (1876), 547. Meyer, *Ber.*, 45 (1912), 1609-33. Ipatiew, *J. Chem. Soc.*, 39 (1907), 681. Smith and Lewcock, *J. Russ. Phys.* -1 (1912), 1453-58. Zanetti and Egloff, *J. Ind. Eng. Chem.*, 9 Cobb and Dufton, *Chem. Trade. J.*, 63 (1918), 197-8.

The general reaction tendency in the aromatic series is such that monocyclic compounds of high molecular weight upon thermal treatment yield monocyclic substances of lower molecular weight. At the same time a tendency for the formation of polycyclic compounds is exhibited.

ADDITIONAL REFERENCES ON AROMATIC HYDROCARBONS

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Armstrong and Miller, *J. Chem. Soc.*, 49 (1886), 74-93.
Haber, F., *J. Gasbel*, 39 (1886), 377-82, 395-99, 435-39, 452-55, 799-805, 813-18, 830-34.
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Engler and Lehman, *Ber.*, 30 (1897), 2365-68.
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Jones, D. T., *J. Chem Soc.*, 107 (1915), 1582-87.
Egloff and Twomey, *J. Phys. Chem.*, 20 (1916), 121-150.
Egloff and Twomey, *J. Phys. Chem.*, 20 (1916), 515-21.
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Fisher, F., and Niggermann, H., *Ber.*, 49 (1916), 1475-82.
Jones, D. T., *J. Soc. Chem. Ind.*, 36 (1917), 3.
Zanetti and Egloff, *J. Ind. Eng. Chem.*, 9 (1917), 474-8.
Egloff, *Met. Chem.*, 16 (1917), 259-63.
Egloff and Moore, *J. Ind. Eng. Chem.*, 9 (1917), 40.
Wheeler, A. S., *J. Ind. Eng. Chem.*, 10 (1918), 359-60.
Meyer, H., and Hofman, A., *Montash*, 39 (1918), 107-28.
Maihle, A. J., *Usines Gaz.*, 44 (1920), 353-5.
Mahood, S. A., *J. Ind. Eng. Chem.*, 12 (1920), 1152-55.
Fisher, F., and Schrader, H., *Brennstoff Chem.*, 1 (1920), 4-6, 22-24.

The Influence of Hydrogen and Inert Atmospheres on the Thermal Reactions of Hydrocarbons.

The influence of hydrogen and inert atmospheres on the thermal reactions of hydrocarbons is a matter of importance to both the producer and the user of motor fuels. The presence of hydrogen, of methane, or other products of the thermal decomposition has an influence on the course of the thermal reactions. This may be chemical; or it may be due to the increase in volume, and, as a consequence thereof, the change in concentration, and also of the duration of heating. Furthermore the low molecular weight gases serve as energy carriers. The light molecules strike the walls of the heating vessel and then dart out again into the reacting vapors to give up their kinetic energy to the slower moving molecules. Thus, as a consequence of the dilution of the hydrocarbon vapors by inert molecules, fewer contacts take place between the heating-vessel wall and the hydrocarbon molecules. Since the material of the wall generally exerts some catalytic effect the fewer the contacts the less the destructive decomposition. This is in all probability the explanation of the "protective" action of inert gases.

The gas manufacturer has long recognized that better results are obtained when gas-oil is decomposed in "blue" water-gas than when

the oil-gas is made separately and then mixed with "blue-gas." The oil refiner has not generally adopted similar methods in his cracking processes, though there are at least two processes used commercially that employ steam as an inert medium. These are the processes of Greenstreet and of the New Process Oil Company. Numerous other patents on processes involving the use of steam or hydrogen have been issued.

The connection between the use of inert atmospheres and the utilization of motor fuels is possibly less evident. However, concurrent with the process of oxidation occurring in the cylinders of an explosion motor is the process of thermal decomposition and dissociation. The air, and the hydrogen and methane formed during the decomposition, act either as inert gases or take part directly in the succession of chemical changes. The ultimate result is influenced profoundly by the presence of these substances.

It is to be regretted, therefore, that our knowledge of the effect of inert gases or of gases such as hydrogen or methane that may have direct chemical effects is so limited.

Bone and Coward[108] have studied the decomposition of ethane in nitrogen and hydrogen. Mixtures of the proportions 1 $C_2H_6 : 3N_2$ and 1 $C_2H_6 : 3H_2$ were heated at 800° C. for one hour. The ethane in each instance was completely decomposed, the ultimate products being carbon, hydrogen, and methane. Eighty per cent of the original carbon content of the hydrogen-ethane mixture appeared in the products as methane. This was 2.27 times as much methane as was formed in the case of the ethane-nitrogen mixtures. Similar results were obtained when mixtures of ethylene with nitrogen or hydrogen were heated at 800° C. for an hour. In this instance 3.15 times as much methane was formed in the hydrogen mixture as in the nitrogen mixture. Their results on the decomposition of acetylene are also of interest. At 800° C. the decomposition products from an hour's heating of acetylene contained 43 per cent of methane. This is difficult to explain except on the basis of the hydrogenation of acetylene by the hydrogen formed in the early part of the reaction period. This was confirmed by the fact that when mixtures of the composition 1 $C_2H_2 : 3N_2$ and 1 $C_2H_2 : 3H_2$ were heated one hour at 800° C. the products from the acetylene-hydrogen mixture contained 4.85 times as much methane as the products from the acetylene-nitrogen mixture.

The results of R. Meyer[109] are confirmatory of those of Bone and Coward in so far as the decomposition of acetylene alone or in atmospheres of hydrogen is concerned.

The protective action of gases is the basis of the Del Monte[110] process of coal carbonization. The inert gases are circulated through the coal gas retorts, thus preventing excessive decomposition.

Hempel[111] studied the gasification of oils in hydrogen and in

[108] *J. Chem. Soc.*, 93 (1908), 1197-1225.
[109] *Ber.*, 45 (1912), 1609-1633.
[110] *J. Fr. Inst.*, 174 (1912), 1-33.
[111] *J. Gasbel*, 53 (1910), 53-58, 77-83, 101-105, 137-141, 155-165.

carbon monoxide. The gas-vapor mixture was led through a tube 16 inches long heated by a row of Bunsen burners. The rate of oil feed was 1.6 to 2.0 grams of oil per minute. A dimunition of volume 15 per cent took place when hydrogen was introduced in the ratio of $1H_2:2$ oil-gas. The gaseous products made in the presence of hydrogen showed a 15 per cent gain in heat of combustion over the simple oil-gas. The separation of carbon was less, and the tars more fluid in the hydrogen-oil-vapor experiments.

From very limited evidence Hempel concluded that the cracking of oils in atmospheres of carbon monoxide or nitrogen caused no change in the volume of gas produced from the oil. The decomposition was of a somewhat different nature, however, as the gas formed contained less methane and more ethylene and other olefins.

Whitaker and Rittman[112] noted that the quantity of gas formed from a given weight of oil increased when the oil was decomposed in atmospheres of hydrogen. The quality of the gas was also improved, and the tar and carbon formation lessened. More hydrogen entered into combination at ordinary pressure than when the pressure was reduced to 0.75 pounds absolute.

The influence of hydrogen on the thermal reactions of hydrocarbons was studied by Whitaker and Leslie.[113]

So far as the influence of hydrogen on the thermal reactions of paraffin hydrocarbons is concerned this work is the most exhaustive that has ever been attempted. The furnace and accessory apparatus used was designed and built by Doctors M. C. Whitaker and C. M. Alexander, and was used by them in studying the manufacture of oil-gases. Since this furnace was so easily controllable and so satisfactory for experimental purposes the details of its construction are shown in Figures 95 and 96.

The heating was effected by the passage through the carbon resistance tube of a 60-cycle alternating current from a 50 K.W. generator. The resistance tube was 38.5 inches long and one inch in internal diameter.

Figures 97 and 98 show the results obtained when a paraffin base kerosene of 0.800 sp. gr. and of 150 to 265° C. boiling range was decomposed alone and in atmospheres of hydrogen. The volumetric ratios of oil-gas to hydrogen approximated $1H_2:2$ oil-gas and $2H_2:1$ oil-gas. The temperatures are indicated in the Figures. The results are expressed as cubic centimeters (0° C., 760 mm.) of the various gaseous hydrocarbon substances formed from each cubic centimeter of oil.

The presence of the hydrogen in the oil-gas may obviously have at least three effects.

[112] *J. Ind. Eng. Chem.*, 6 (1914), 472-79.

[113] Dissertation submitted by E. H. Leslie in partial fulfillment of the requirements for the Doctor's Degree, Columbia University, 1916. *J. Ind. and Eng. Chem.* (An abstract of the experimental work published jointly with Dr. M. C. Whitaker under whom this work was done.) 8 (1916), 593-601, 684-695.

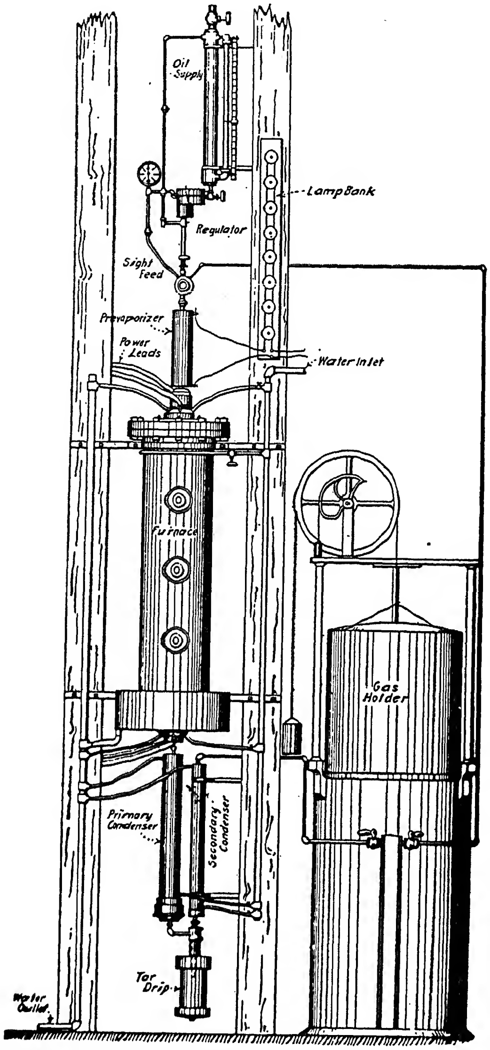

FIG. 95.—Apparatus for Studying the Thermal Reactions of Hydrocarbons.

1. Dilution — whereby the partial pressures of all gaseous substances are decreased.

2. Increase in total volume—whereby the time of heating the hydrocarbon molecules is less than in making straight oil-gas.

3. Hydrogenation, or reaction of the various hydrocarbons with hydrogen.

The diminution of the partial pressures tends to favor those reactions that result in the formation of a larger number of molecules.

The decrease in the time of heating causes a less extensive decomposition.

The chief result of hydrogenation is the formation of a larger proportion of methane as a result of such reactions as:

$$C_2H_6 + H_2 \longrightarrow 2CH_4$$
$$C_2H_4 + 2H_2 \longrightarrow 2CH_4$$

Though it is difficult to show quantitatively the effect of these three factors, the effect of the last two is shown qualitatively in the accompanying figures.

At 621° C. the lessened time of heating causes a smaller formation of hydrocarbons in the case of the hydrogen oil-gas mixtures, except at very low oil rates, or conversely, when the time of heating was long, and a mixture.

At 723° C. 1 H_2 : 2 oil-gas, the same effect is seen in the case of the formation of methane and of illuminants (gas soluble in fuming H_2SO_4). But ethane is formed in larger quantity in the hydrogen gas mixture than in the oil-gas alone. The "protective" influence of hydrogen, already explained for inert gases in general, and the lessened

time of heating are responsible for this phenomenon. Apparently a small amount of ethane is formed readily from the oil, but this gas is easily decomposed thermally.

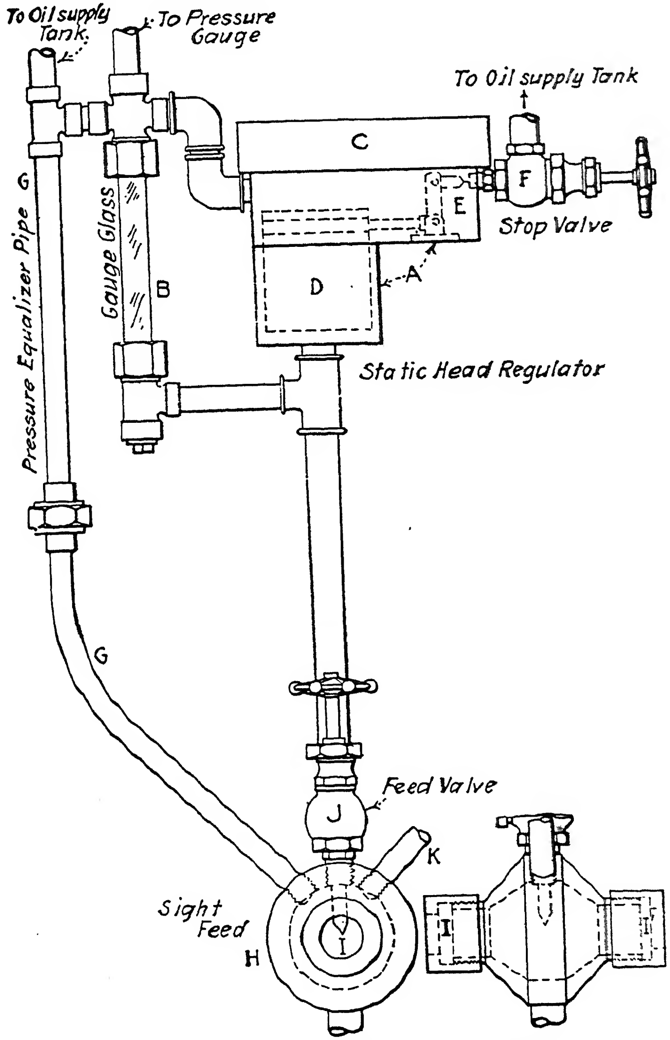

FIG. 96.—Constant-Head Feed Device.

All of these effects are accentuated at 723° C. when the proportion of hydrogen is increased to $2H_2:1$ oil-gas. The marked increase of ethane to a maximum at an oil feed-rate of 5 cc. per minute is notable.

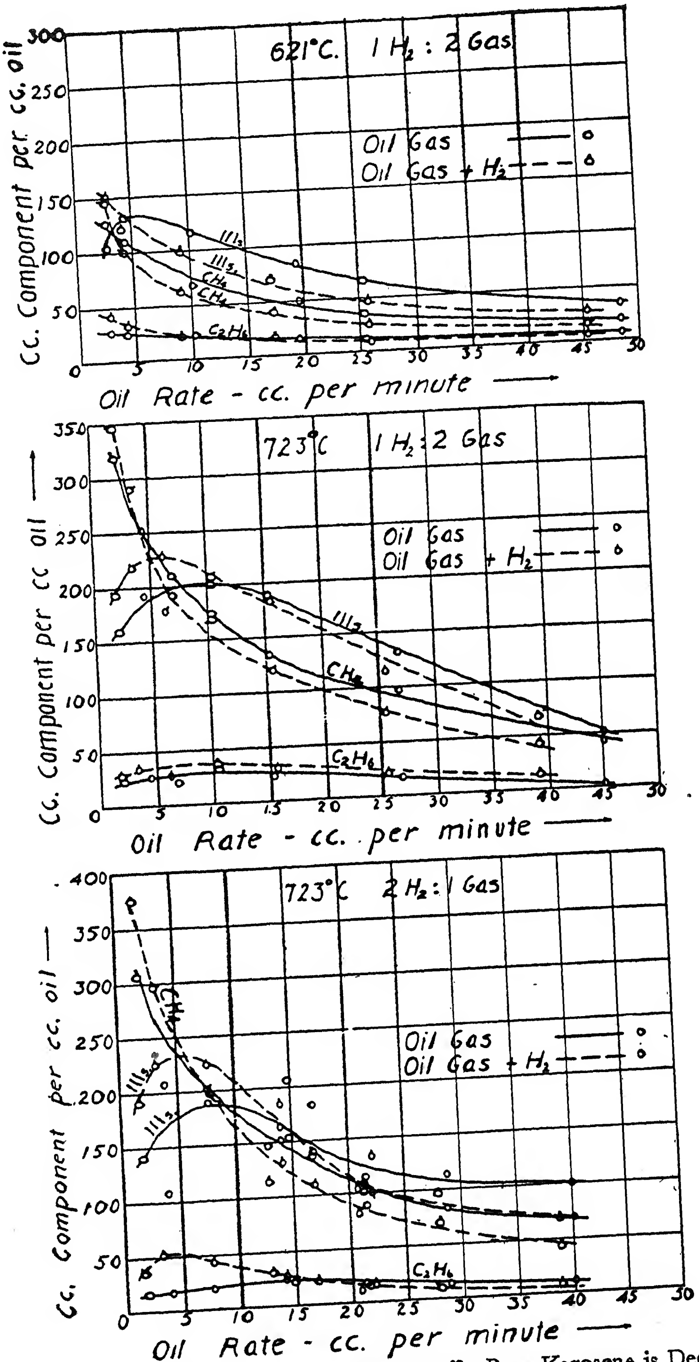

FIG. 97.—Gaseous Products Formed when Paraffin-Base Kerosene is Decomposed Alone or in Hydrogen at 621° C. and at 723° C.

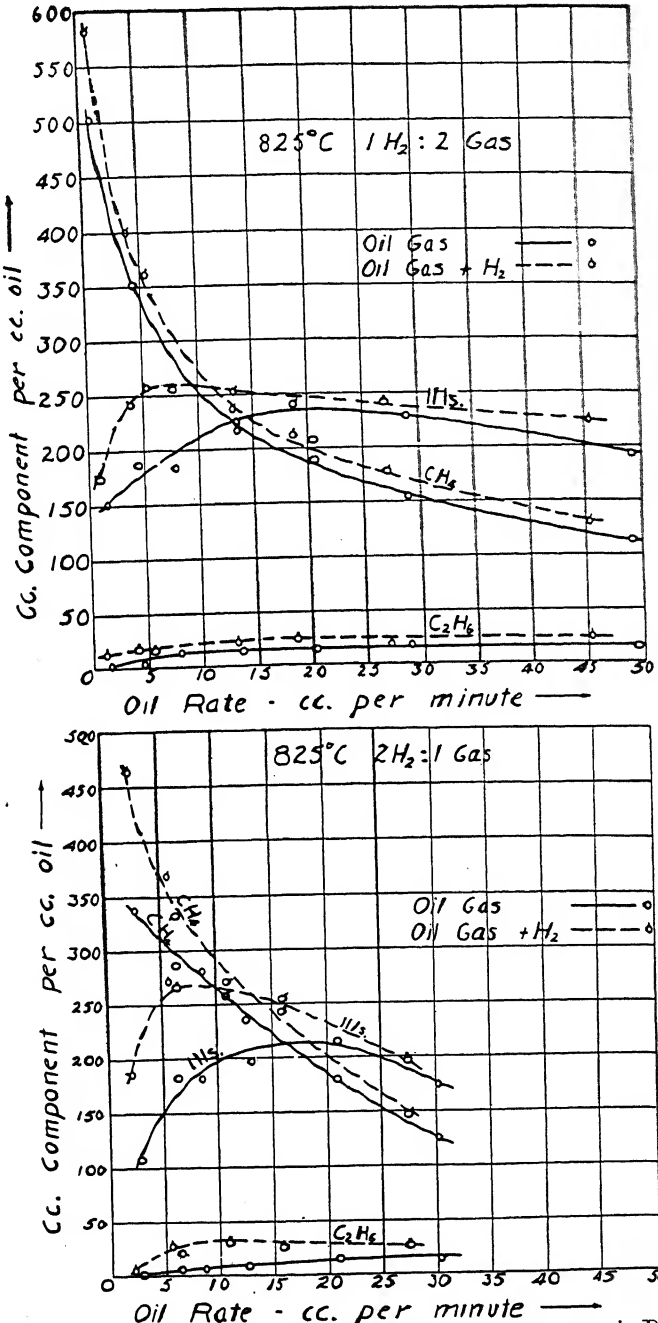

FIG. 98.—Gaseous Products Formed when Paraffin-Base Kerosene is Decomposed Alone or in Hydrogen at 825° C.

This is possibly due to hydrogenation of ethylene. The lesser formation of ethane in the hydrogen-gas experiments in which the oil-rate was over 20 cc. per minute indicate that the time of heating in these runs was insufficient for the extensive occurrence of those reactions that form ethane.

The use of higher temperatures somewhat changes the relationships. At 825° C. reaction rates are much more rapid than at 723° C. The lessened time of heating due to admixture of the hydrogens, therefore, has a beneficial effect.

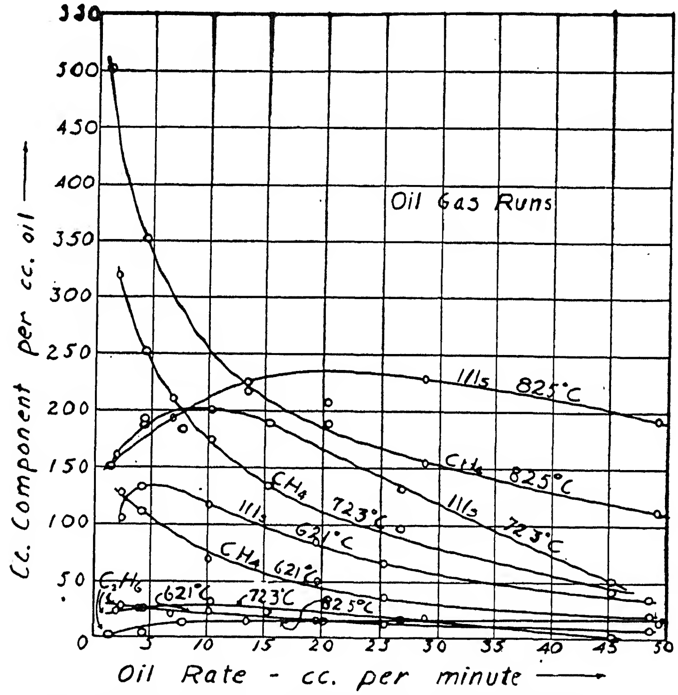

FIG. 99.—Formation of Ethane, Methane, and Gaseous Olefins from Paraffin-Base Kerosene.

Figure 99 shows that the extent of the formation of ethane, methane, and gaseous olefins or "illuminants" at various temperatures and oil-rates, and also shows the nicety of adjustment between the effects of temperature and time of heating.

Figure 100 shows the total number of cc. of methane, ethane, and illuminants formed from each cubic centimeter of oil at 621° C., 723° C., and 825° C., at varying rates of oil-feed. The marked increase in the amount of carbon appearing in the products in gaseous form shows that at the lower oil-rates destructive decomposition has been lessened, and that reactions have taken place between the hydro-

carbons and the hydrogen. This is confirmed by Figure 101 showing approximately the number of cubic centimeters of hydrogen absorbed during the passage of the hydrogen-gas mixtures through the reaction tube.

A most interesting investigation of the reactions of benzene, and toluene, in vapor form, alone, and in the presence of either hydrogen or nitrogen, has been made by S. F. Dufton and J. W. Cobb.[114]

The gas-vapor mixtures were passed through a coke column in an electrically heated quartz tube 1⅛ inches in diameter. The time of contact was approximately 12 seconds.

Benzene in nitrogen started to form condensation products at 500° C.

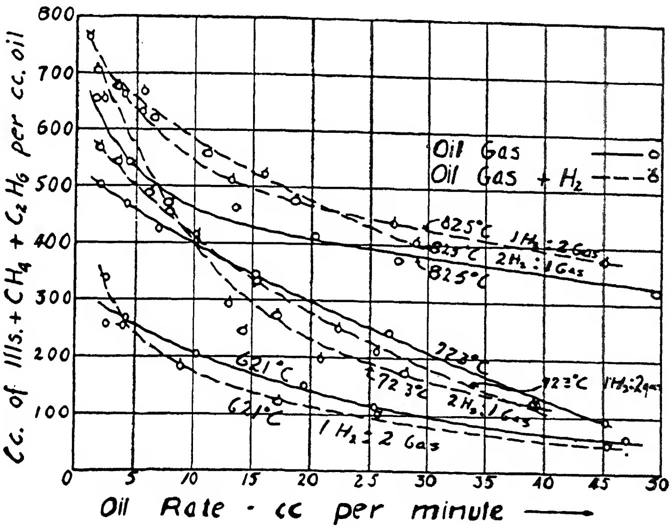

FIG. 100.—Total Volume of Hydrocarbon Gases Formed per Cubic Centimeter of Paraffin-Base Kerosene Decomposed at 621° C., 723° C., and 825° C.

Hydrogen was eliminated, and the first product was diphenyl. At 750° C. the reactions are much more complex, and at 920° C. free carbon is formed in quantity. When benzene is mixed with hydrogen ($12H_2 : 1C_6H_6$-vapor) molecular condensation and decomposition were almost completely prevented at 750° C. The reversibility of the diphenyl condensation was proved by passing diphenyl and hydrogen over the coke at 750° C. Benzene was found.

Toluene mixed with nitrogen in varying proportions undergoes molecular condensation at 550° C. The products are stilbene and probably ditolyl. As in the case of benzene, hydrogen decreased the molecular condensation but reduced toluene to benzene and methane. This latter reaction was proved reversible by passing benzene and

[114] *Gas J.*, 150 (1920), 588-591.

methane over coke at 750° C., when toluene was formed in small quantity.

Xylene and cresol in hydrogen both yield toluene and benzene, and

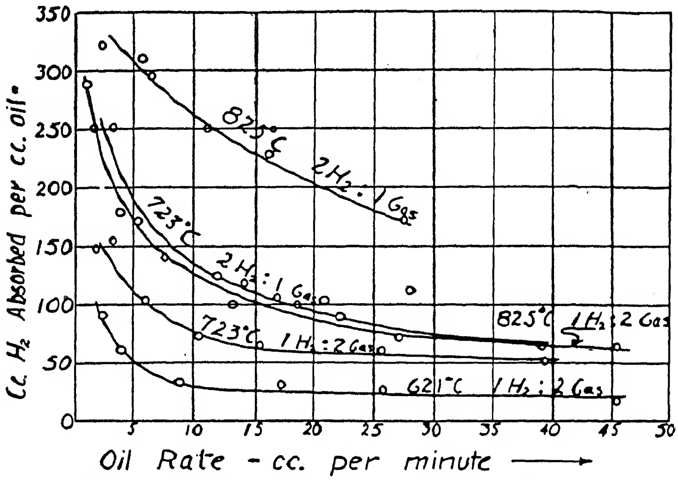

FIG. 101.—Hydrogen Absorbed During Thermal Treatment of Paraffin-Base Kerosene Under Various Conditions.

also undergo molecular condensation. The important influence of the atmosphere in which hydrocarbon reactions occur is clearly demonstrated. The effect of hydrogen is markedly different from that of nitrogen.

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The Effect of Pressure on the Thermal Reactions of Hydrocarbons.

The effect of pressure on the thermal reactions of hydrocarbons is less clearly understood than the effect of changing any of the other conditions. This statement is made advisedly, and in spite of the fact that several writers have ascribed various results to changes in pressure.

Pressure may conceivably alter the results by increasing the concentration of substances reacting in the gaseous phase, by increasing the time of heating, and by shifting the equilibrium point of the reac-

tions. The change in concentration directly influences velocity of reactions, for rate of reaction is proportional to the first or some integral higher power of the concentration. Consider the reversible reaction

$$A_2B \rightleftarrows 2A + B$$

If the instantaneous velocity of the reaction $A_2B \longrightarrow 2A + B$ is represented by V_{t1}, and that of the reaction $2A + B \longrightarrow A_2B$ by V_{t2} these velocities may be expressed in terms of the concentration of the reacting substances as follows:

$$V_{t1} = K_1 \cdot C_{A_2B} \qquad V_{t2} = K_2 \cdot C_A^2 \cdot C_B$$

Where K_1 and K_2 are constants, and C_{A_2B}, C_A, and C_B are the concentrations of the three substances A_2B, A, and B.

If the pressure on this system were doubled the expressions for these instantaneous velocities would be

$$V_{t1} = 2 \cdot K_1 C_{A_2B}$$

$$V_{t2} = K_2 \cdot (2C_A)^2 \cdot 2C_B = 8K_2 \cdot C_A^2 \cdot C_B$$

The velocity V_{t2} has been increased four times as much as the velocity V_{t1}. Thus it is seen that an increase in pressure favors reactions resulting in combination of several molecules into fewer molecules.

It is conceivable that the effect of pressure on the instantaneous velocities may be sufficient to change the proportions of the substances found in an hydrocarbon-system.

Secondly it is a well-known fact that a change in the time of heating produces variations in the relative amounts of the products of a reacting hydrocarbon-system. To state the proposition in another way, the hydrocarbon-system is not in equilibrium, that is, it is not in a condition that is independent of the further passage of time. This has been shown by many investigators. Change of pressure may thus indirectly affect the extent of the chemical change. This in my opinion is the main effect of a change in the pressure on a reacting hydrocarbon-system.

The use of pressure is of practical advantage in vapor-phase cracking since the size of the apparatus may be kept within reason, and yet allow a sufficient time for the reactions.

The effect of pressure on the equilibrium point of the reactions is of little importance since hydrocarbon-systems do not reach, nor even approach, equilibrium. Increase in pressure would tend to shift the equilibrium in such a manner that those reactions would be favored that result in the formation of fewer molecules.

In the liquid-phase process the application of pressure serves a somewhat different purpose, namely, that of keeping the hydrocarbon oil in the still or reaction vessel. In order rapidly to volatilize the oil that is to be cracked, the vapor tension of the volatil components of the oil must equal the vapor pressure of these components of the

vapor-phase. The application of pressure therefore allows the use of higher temperatures in the still, and in this manner distillates of moderate volatility such as gas-oil can be held in the reaction vessel at temperatures of 650 to 750° F., by using pressures of only 75 to 80 lbs. gage. I am of the opinion that the effect of pressure, per se, on the course of the reactions in the body of the liquid, in the vapor above the liquid, or in the condenser, is negligible.

The literature on the subject of the decomposition of oils is filled with references to the use of pressure, yet in no instance that has come to my attention has the effect of pressure been differentiated from the effect of the time-factor. For this reason the citation of experimental proof of the effect of pressure, as such, is impossible at present. Experimental work must be carried out in such a manner that the time-factor and the temperature are the same in each experiment. If the pressure had an effect on the reactions it would influence the volume and hence the time-factor. Only by a series of approximations could the experimental conditions be adjusted so that the time-factor in all would be the same, and the effect of pressure, as such, be ascertained.

The Effect of Catalysts on the Thermal Reactions of Hydrocarbons.

The use of catalysts in the production of motor fuels has been limited, and it is probably true that the aluminum chloride processes as developed by McAfee and by G. W. Gray, and the vapor-phase process of Ramage in which iron-oxide is used in the tubes, are the only catalytic processes that have attained any degree of commercial success. However, it is entirely possible that the future will see further development in this direction.

Catalysts may be applied to the vapor-phase cracking processes, or to the liquid phase processes. Recent experimental work under my observation leads me to believe that catalysts may be applied to advantage in the utilization of fuels in explosion or internal combustion engines.

Effect of Catalysts on the Thermal Reactions of Vaporized Hydrocarbons.

If one were to look to the patent literature for the facts regarding ·ffects of catalysts on the reactions of vaporized hydrocarbons he l be led to believe that many catalysts had been successfully used. review of a number of these processes the reader is referred to ınd Meigs, "Gasoline and Other Fuels." But the verdict of ment is rather different. Two main types of catalysts have been l, metals, and metal oxides.

e catalytic activity of nickel, cobalt, and iron in the thermal positions was observed long ago, and is now generally recognized. ose metals nickel is the most active catalyst. The rate of the ms is increased, and also the result obtained is different when

oil-vapor is decomposed in the presence of these metals. However, from a practical standpoint the nature of the reactions is undesirable. The formation of carbon, hydrogen, and methane is extensive. The tendency toward dehydrogenation is especially marked. But in spite of the undesirable characteristics of the products formed, and of the technical difficulties resulting from deposition of carbon, numerous processes are patented that in one way or another involve the use of these catalysts.

The work of several investigators should be mentioned in connection with the use of metal catalysts. In 1866 Berthelot noticed that acetylene was rapidly decomposed into carbon and hydrogen in the presence of finely divided iron. Later Moissan and Moreau [115] made similar observations, and found that cobalt showed catalytic activity similar to that of nickel. Sabatier and Senderens [116] passed pure dry ethylene over freshly reduced nickel at 300° C. and upwards. The products were carbon, hydrogen, methane, and ethane in varying proportions. The higher the temperature the greater was the formation of hydrogen. Ostromisslenski [117] studied the reactions occurring when vaporized Russian petroleum was passed over nickel at 600 to 700° C. The oil was completely decomposed into methane, hydrogen, and a carbonaceous residue.

The decomposition of a Russian oil in the presence of iron gauze as catalyst was studied by Ostromisslenski and Burzhanadze.[118] They observed an extensive decomposition at 700° C., and found 10.9 per cent benzene and 3 per cent of naphthalene in the liquid products.

Ubbelohde and Woronin [119] have shown that when nickel was used as a catalytic agent a crude oil from Baku split off hydrogen at 180° C. This was quite in contrast to the temperature required (470 to 480° C.) for the initial formation of hydrogen from a paraffin oil, when no catalyst was present, as shown by Engler and Spanier.[120]

Tausz [121] found that hexamethylene and hexane were dehydrogenated by active palladium at a temperature of 300° C.

J. E. Zanetti,[122] and Zanetti and Leslie,[123] found that nickel and iron exerted a marked catalytic influence on the decomposition of the ethane, propane, and butane fractions of natural gas condensate. The decomposition into carbon and hydrogen was promoted and the formation of aromatic hydrocarbons lessened. Copper had little if any effect of this sort.

J. G. Davidson [124] in a study of the formation of aromatic hydrocarbons from natural-gas condensate found that nickel, cobalt, and

[115] *C. r.*, 122 (1896), 124.
[116] *C. r.*, 124 (1897), 616-18.
[117] *J. Russ. Phys. Chem. Soc.*, 42 (1910), 195.
[118] *J. Russ. Phys. Chem. Soc.*, 42 (1910), 195.
[119] *Pet.* (Berlin), 7 (1911), 9.
[120] *D. Erd.*, 574-6.
[121] *Chem. Ztg.*, 37, 334.
[122] *J. Ind. Chem.*, 8 (1916), 674-8.
[123] *J. Ind. Eng. Chem.*, 8 (1916), 777-9.
[124] *J. Ind. Eng. Chem.*, 10 (1918), 901-10.

iron catalyzed the decomposition of the hydrocarbons into carbon and hydrogen.

Tausz and Putnoky[125] investigated the dehydrogenation of hydrocarbons by means of palladium-black. Cyclohexane was quantitatively dehydrogenated by an active catalyst at 300° C., and isopentane, hexane, heptane, and octane started to dehydrogenate at 300° C.

Recently the decomposition of acetylene in the presence of several metallic catalysts has been investigated by E. Tiede and W. Jenische.[126] The metals most active as catalysts were iron, cobalt, nickel, copper, and manganese. The difference in catalytic activity were attributed to the varying solvent powers of the metals for hydrogen.

The effect of the metals as catalysts may be summarized by the statement that nickel, cobalt, iron, platinum, and palladium lower the temperature of decomposition of the hydrocarbons, and promote the formation of hydrogen and methane, carbon, and highly carbonaceous residues. These results are undesirable, and it is therefore difficult to see how the use of these metals can be made the basis of workable processes.

The Use of Oxide Catalysts in the Thermal Decomposition of Hydrocarbons.

The decomposition of hydrocarbons in the presence of oxide catalysts has not been studied so extensively as has the effect of metal catalysts on hydrocarbon reactions. Ubbelohde, St. Philippide and Woronin[127] studied the decomposition of a heavy oil (sp. gr. 0.900) in the presence of kaolin, alumina, fuller's earth, nickel, and no catalyst. The decomposition temperature was lowered in the presence of the catalyst, but few conclusion can be drawn from this work.

Ipatiew and Dogelevitsch[128] passed hexane and hexamethylene vapor through an iron tube containing alumina at a temperature of 650 to 700° C. They found the decomposition was promoted by alumina. The isomerization of six-carbon ring compounds is also catalyzed by alumina.

The catalytic activity of several metal oxides has recently been studied by E. H. Leslie and R. B. Werey.[129] The effect of pumice stone and of the oxides of aluminum, iron (Fe_2O_3), cerium (CeO_2), copper (CuO), vanadium (V_2O_5), and chromium (Cr_2O_3) mounted on pumice stone was investigated. The oil used was a Pennsylvania paraffin-base kerosene. It was first vaporized, and then passed through a brass lined iron tube filled with catalyst for five inches of its length. The temperature in all experiments was 500° C.

The investigation showed that alumina exerted a small catalytic influence. Ferric oxide and chromium oxide also were not without influence on the reactions. All of the others were inert. Though the

[125] *Ber.*, 52 B (1919), 1573-83.
[126] Brennstoff, *Chem.*, 2 (1920), 5-8. *J. Soc. Chem. Ind.*, 40 (1921), 111A.
[127] *Pet.*, 7 (1911), 1233-38.
[128] *J. Russ. Phys. Chem. Soc.*, 43, 1431-6.
[129] Unpublished data.

effect of alumina was small the conclusion should not be drawn that the effect could not be utilized in commercial practice where the oil-vapor could be made to pass over the catalyst in long tubes.

Aluminum Chloride and Other Metal Halides as Catalysts.

The use of aluminum chloride as a catalyst forms the basis of the processes of McAfee and of Gray. The anhydrous salt is added to the oil and the resultant mixture distilled. These processes or others similar to them have not come into general use on account of the high cost of aluminum chloride. It is reasonable to suppose that this obstacle will be overcome in time.

So far as I am aware an exact explanation of the catalytic action of aluminum chloride in the treatment of petroleum oils for the production of lighter distillates is still lacking. Consideration of the experimental evidence inclines one to accept an explanation similar to that given Falk[130] in his discussion of theory of the Friedel-Crafts reaction. The viewpoint adopted is essentially that of Menschutkin, Boeseken, and Schmidlin and Lang. The formation of a ternary compound that is capable of dissociation in several ways is postulated. For example the reaction of ethyl chloride, benzene, and anhydrous aluminum chloride may be formulated:

$$\left(\begin{array}{l} C_2H_4 \\ C_6H_5H \\ HCl \\ AlCl_3 \end{array}\right) \begin{array}{ll} \rightleftarrows \begin{pmatrix} C_2H_4 \\ HCl \end{pmatrix} + C_6H_5H + AlCl_3 & \text{(a)} \\ \rightleftarrows \begin{pmatrix} C_2H_4HCl \\ AlCl_3 \end{pmatrix} + C_5H_6H & \text{(b)} \\ \rightleftarrows \begin{pmatrix} HCl \\ AlCl_3 \end{pmatrix} + C_6H_5C_2H_5 & \text{(c)} \end{array}$$

The reaction is ordinarily considered as a means of preparing ethyl benzene, so the equilibrium must be such that reaction "c" predominates.

It is not difficult to conceive of some similar mechanism for the reactions in which hydrocarbons of almost any nature give rise to paraffins and polymethylenes when treated with anhydrous aluminum chloride. Intermediate compounds are formed and then dissociate, possibly in the vapor state, as has been suggested by McAfee[131] to form low boiling saturated hydrocarbons and highly carbonaceous residues.

C. Gangloft and W. E. Henderson[132] have isolated numerous compounds of olefins and $AlCl_3$, formed when the hydrocarbon was passed through or added to a solution of anhydrous aluminum chloride in absolute ethyl or methyl alcohol. The compounds formed from several olefins and from acetylene are given herewith.

[130] *Chemical Reactions*, pp. 99-105.
[131] *Met. Chem. Eng.*, 13 (1915), 92-97.
[132] *J. Am. Chem. Soc.*, 38 (1916), 1382-4; (1917), 1420-7.

Acetylene $\longrightarrow$ $AlCl_3.C_2H_2.2(C_2H_5OH)$
Ethylene $\longrightarrow$ $AlCl_3.C_2H_4.2C_2H_5OH$
V-Butylene $\longrightarrow$ $AlCl_3.(CH_3)_2C = CH_2.2CH_3OH.H_2O$
β-iso-Amylene $\longrightarrow$ $AlCl_3.C_5H_{10}.CH_3OH$.

All of the compounds were difficult to prepare and analyze. They do not claim that these compounds are exactly those formed in the decomposition of petroleum oils by means of anhydrous aluminum chloride, but suggest that the compound formation in the latter case is analogous. The combination of $AlCl_3$ with the olefins explains the nearly complete absence of these hydrocarbons from the volatil distillates formed in cracking.

When amylene is heated with aluminum chloride, methylcyclobutane and higher boiling polymethylenes are formed along with larger quantities of paraffin hydrocarbons. This has been demonstrated by Aschan[133] and by Engler and Routala.[134] The latter investigators showed that the fractions of the product boiling below 175° C. were largely paraffinic. Naphthenes were present in increasing quantity in the fractions boiling above 175° C. Also olefins to the extent of 4 to 12 per cent were present in these higher boiling portions.

The work of M. Freund[135] on the action of aluminum chloride on turpentine oil is of interest as illustrating the formation of paraffins and polymethylenes from unsaturated cyclic compounds. The products were similar, qualitatively at least, to those formed from straight-chain olefins. The lower boiling fractions were largely paraffins, but as the boiling point rose a larger proportion of the distillate was naphthenes.

Pictet and Lerczynska[136] studied the action of anhydrous aluminum chloride on Galician, Austrian, American, and Caucasian lubricating oils, burning oils, and vaseline. The results were apparently independent of the rate of distillation and the pressure. Variations depended on the nature of the oil treated. The light benzine, b.p. 40° C. to 140° C. obtained from a Baku lubricating oil was carefully studied. It was a colorless liquid, sp. gr. 0.72, showed no fluorescence, had a pleasant odor, contained no Cl or S, and had the elementary composition C = 84.45 per cent, H = 15.44 per cent. The fractions contained both paraffins and naphthenes.

The heavy residue remaining in the apparatus after the distillation had been carried to a temperature of 400° C. contained 92.2 per cent C. and 7.4 per cent H., thus approximating C_nH_{2n}.

The explanation offered for the reaction of $AlCl_3$ on Baku petroleum s that a compound $\underbrace{CH_2CH_2CH_2CH_2CH_2CH} — CH_2 — (CH_2)_4 —CH_3$, ypical of the naphthenes in this oil, splits to hexane and

$$\underbrace{CH_2CH_2CH_2CH_2CH = CH}.$$

'nn., 324 (1902), 26.
: (1909), 4610-20; 43 (1910), 388.
(1914), 411-20.
19 (1916), 326-34.

The latter substance polymerizes to form the heavy asphaltic substances composing the still residue.

The effect of other metal chlorides was studied, and it was shown that the action of $FeCl_2$ and $FeCl_3$ was similar, but less rapid and complete, than that of $AlCl_3$. $CaCl_2$, $ZnCl_2$, $CrCl_2$, $SnCl_2$, $CuCl_2$ and $HgCl_2$ were without effect.

Egloff and Moore[137] studied the effect of passing HCl gas or Cl_2 gas over several metals and nonmetals immersed in a Pennsylvania kerosene. They found the following percentages of distillate to 150° C. were formed.

Gas Passed	Catalytic Metals or Non-Metals							
	Mg	Zn	Na	Al	Si	S	P	Se
HCl	1.0	4.9	5.3	37.3	...	...	...	...
Cl_2	0.3	...	...	15.9	0.6	0.7	1.7	5.3

Aluminum is thus seen to be the most active catalyst, and more than twice as effective when the gas passed through the reaction mixture was HCl rather than Cl_2.

FURTHER REFERENCES ON EFFECT OF CATALYSTS ON THERMAL REACTIONS OF HYDROCARBONS

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Kuznetov, N., *Ber.*, 40 (1907), 2871.
Maihle, A., *Chem. Ztg.*, 32 (1908), 229, 244.
Ipatiew and Dowgelewitsch, *Ber.*, 44 (1911), 2987.

For a list of patents covering processes of treating oils with the aid of catalysts see Lomax, Dunstan, and Thole,[138] and also Ellis and Meigs.[139]

ADDITIONAL REFERENCES: ACTION OF $AlCl_3$ ON OLEFINS

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Anchianowsky, *Ber.*, 12 (1879), 853.
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Steele, *J. Chem. Soc.*, 83 (1903), 1470.
Ipatiew and Routala, *J. Russ. Phys. Chem. Soc.*, 45 (1913), 995-1003.

[137] *Met. Chem. Eng.*, 15 (1916), 67-9.
[138] *J. Ind. Eng. Chem.*, 9 (1917), 884.
[139] "Gasoline and Other Motor Fuels."

Chapter IX.

Cracking Processes.

Cracking processes are those processes designed to convert hydrocarbons of medium to high molecular weight into hydrocarbons of lower molecular weight. Unfortunately it is impossible to produce the lower boiling products without concurrent formation of high boiling substances, for processes of polymerization and condensation are at work as well as those of decomposition and dissociation. The extravagant claims sometimes heard that 75 per cent to 90 per cent of a heavy oil can be converted into gasoline are seen to be ridiculous when one remembers that both low and high boiling hydrocarbons are always produced by cracking.[1]

Many hundreds of patents covering processes or apparatus for cracking have been issued. In fact, the Patent Office has developed a new form of indoor sport along this line. Among the many patents a few have proved to cover processes of real value. It is not my purpose to take up all or even a small number of the issued patents. The discussion will be limited to those processes whose merit has been proved by commercial use or which have attracted more than passing interest. The United States patents covering these processes are given, but none of the accompanying statements should be construed as opinion on the validity of the patents. These are all assumed to be valid, and not in conflict one with another. This is apparently not the true state of affairs, for at the time of this writing, the Standard Oil Company of Indiana is defendant in behalf of the Burton Process in suit brought by the Universal Products Company for infringement of the Dubbs'

[1] The name "cracking" as applied to these processes has met the disapproval of some writers who prefer more liquid sounding or more pretentious designations such as "pyrolysis" or "pyrogenesis." I feel, however, that the word "cracking" is a peculiarly apt name in that it connotes the desired result. True, it does not suggest that a process of polymerization takes place simultaneously with decomposition. But, for that matter, neither do the other names. To me it appears quite as logical to designate the generation of steam in a boiler as a "pyrogenetic" change. The steam is "born of fire" just as truly as the distillate from the cracking-still or tubes.

The crude distillate produced in cracking plants is usually called "synthetic distillate" or "synthetic crude." While these names are probably not justifiably applicable to the lower boiling portion of the cracking-plant crude, they have the sanction of usage, and without doubt, avoid confusion. The word "synthetic" is used as an adjective in the sense that the distillate has been produced by a chemical process as distinguished from merely being distilled from crude-petroleum. Products separated from crude-petroleum are designated as "straight-run."

patent, the Standard Oil Company of New Jersey has brought suit against the Pure Oil Company which uses the Cross process, owners of the Jenkin's patent claim in suit that the Isom process of the Sinclair Refining Company is the invention of U. S. Jenkins, and the Gulf Refining Company and Texas Company are at legal grips over the aluminum chloride processes of McAfee and of Gray respectively.

Whence Came the Cracking Process?

The manufacturer of gas has cracked hydrocarbons since 1792 when illuminating-gas was made by Wm. Murdock, and the development of the gas industry has in general been based on growing knowledge of hydrocarbon reactions.

In 1855 Professor Silliman of Yale, in a report on the "rock-oil" of Pennsylvania, suggested that decomposition of the oil occurred during distillation. Report has it, although with what authenticity I am not aware, that the "cracking-distillation," used to increase the yield of burning-oils, was discovered by a negligent still-man in Newark in 1861. Upon returning to the still, which he had left some hours before with banked fires, he found the stream of lower specific gravity than when he had left.

In 1865 Young[1a] took out a patent covering the manufacture of burning oils by heating oils under a pressure of 20 pounds. This was followed with patents by Benton,[2] Krey,[3] and Dewar and Redwood[4] covering processes in which petroleum oils were decomposed by heating under pressure. Numerous other patents were issued in this and foreign countries, the majority prior to 1910 covering processes or apparatus for the manufacture of burning oils or aromatic hydrocarbons. Lomax, Dunstan, and Thole[5] have reviewed the subject of patents on cracking processes and reference should be made to their paper. Reference should also be made to "Gasoline and Other Motor Fuels," by Ellis and Meigs, for numerous patent citations.

The great expansion of the automotive industry furnished the impetus for the development of cracking processes designed to convert heavy oils into gasoline. The development of present methods has taken place in the last decade, and the most active work has been done in the last five years. Refiners have been slow to adopt new and unconventional methods partly because precedent and old-line methods constituted the mental stock in trade of many refinery operatives or managers, and partly because of fear of legal action that might be brought by powerful interests that control processes now in use. The chemical engineer is only now taking a proper part in the development of refinery technology. It is to be hoped that his efforts

[1a] E. P. 3345 (1865).
[2] E. P. 1922 (1887), U. S. P. 342,564; 342,565 (1886).
[3] Ger. Pat. 37,728 (1886).
[4] E. P. 10,287 (1889), 13,016 (1890), 5,971 (1891); U. S. P. 419,931, 426,173 (1890); Ger. P. 53,552 (1889).
[5] *J. Inst. Pet. Tech.*, 3 (1916), 36-70. *J. Ind. Eng. Chem.*, 9 (1917), 879-902.

will do much to develop and standardize cracking methods. Furthermore, the legal battles now being waged, or that are in prospect, should clear the air, and result in a delineation of patent rights plain enough to serve as a basis for confident development of the art by refiners, however large or small.

The Importance of Cracking Processes to the Industry.

Whatever may be the ultimate solution of the motor fuel problem, a transitional stage must be involved between present and future sources of supply. For a decade or more, motor fuel must be made largely from domestic and imported petroleum. Whether the tremendous expansion of the automotive industries is necessary or justified is beside the point. The use of motor vehicles has increased apace, and there is no apparent reason for believing that it will not continue, at least moderately, to grow. The profit of the oil-refiner will largely come from the sale of gasoline, and the company that obtains the largest yields of gasoline will be most successful. Grant that alcohol, shale-oil, engine development and other factors will eventually become of great importance. This does not alter the fundamental fact that cracking processes have arrived, and that they are at present the "easiest way" toward a solution of the gasoline problem. It is possible today to obtain 50 to 65 per cent of gasoline even from such heavy crudes as those of Mexico or California.

One-fifth of the gasoline marketed in this country is made by cracking. Possibly, the proportion is somewhat higher than this. The intensive application of cracking processes, both of vapor-phase and liquid-phase types, will allow of doubling the supply of gasoline. True, these methods will not be used so extensively as to accomplish this result at once. The consumer of fuel oils will have to be shown by dollar persuasion that he can use coal to better advantage. In any event, a substantial quantity of fuel oil in the shape of residues from the cracking process will always be available. Possibly the water-gas manufacturer will be forced to go into the liquid-phase cracking business to ensure himself a supply of suitable gas-oil. There will be many economic adjustments of this nature that time and dollar persuasion will iron out. Even the motorist may think more carefully of forty- or fifty-cent gasoline!

'he Future Cracking Process.

Cracking processes in use today require gas-oil or similar middle distillates as raw material. The quantity of these distillates is limited, and unless processes or combinations of processes are developed that will handle the heavy fuel-oils and residuums successfully, the usefulness of cracking methods is definitely limited. The dangers attendant on the excessive deposition of carbon in pressure-stills prohibits the use of heavy oils as raw material in these processes. Also, the forma-

tion of large amounts of tarry substances and carbon prevents the use of heavy oils in vapor-phase plants.

Clearly the real need today is a process that will handle the heavy 50 per cent of Mid-Continent oils, or the 80 per cent residuum of the heavy California, Gulf Coast, or Mexican oils. The problem is not hopeless at all. In fact, at least one combination of processes is now available that will do the work.

What Should a Good Cracking Process Accomplish?

This question is easily answered. A good cracking process is one that quickly, economically, and safely converts 20 to 30 per cent of a heavy oil into a gasoline distillate of desirable volatility and of low olefin content. This result should be obtained in a single treatment of the raw material. By repetition of the process much higher yields should be obtainable.

Economy implies small plant investment as well as low operating costs. Simplicity of design and construction, and speedy conversion, or conversely, large capacity per unit of investment and operating cost, are essential. Complication of operating details to such an extent that highly skilled labor, to say nothing of close technical supervision, is required, is unwarranted. Fuel consumption must be low.

Classification of Cracking Processes.

Cracking processes may be classified into two groups:

1. Processes in which the oil in vapor form is thermally or energetically treated.
2. Processes in which the heat or other form of energy is applied to the oil in liquid form, with some part of the liquid in contact with vapor.

These processes may for short, be loosely designated as vapor-phase and liquid-phase processes.

The use of pressure or of catalysts may be a part of processes of either class.

Vapor-Phase Processes.

Before describing several typical vapor-phase processes, I wish to set down a few general facts gleaned from, and opinions formed during my experience with vapor-phase cracking operations.

Success in vapor-phase cracking depends on careful attention to details both of design and operation. A common error is the use of tubes of three-inch or greater internal diameter. Two-inch or two-and-one-half-inch tubes are most satisfactory. The reason is simple enough. Gases are poor conductors of heat. If large short tubes are used it is impossible uniformly to heat the gases within. On the other hand, cracking-coils made of 2-in. or 2½-in. tubes connected by welded return-bends into coils 200 ft. to 1000 ft. long, offer the best oppor-

tunity for quick and uniform heating. The velocity of the vapor is high, and the flow turbulent. Also, coils of this nature can be so supported within the furnace that the removal of heat from the flue-gases is very effective. The low-temperature portion of the coil can be made to function as a recuperator.

Drawn steel tubes will be found most satisfactory, lap-welded tubes next, and butt-welded tubes least satisfactory. Extra-heavy tubes should be used because of the gradual oxidation of the outside surface, and also of the inside surface if the coil is blown with air to remove carbon. The use of calorized tubes is probably justified. The patents covering the calorizing process are owned by the General Electric Company. The exposed surface of a calorized tube is composed mainly of Al_2O_3 under which is a layer of aluminum, then a layer of iron-aluminum alloy, and finally the steel of the tube. The aluminum oxide protects the tube from oxidation to some extent, and furthermore, carbon does not deposit so readily on the surface of a calorized tube.

The manner of feeding the raw materials is most important. Small variations in rate of feed seriously influence results obtained. The thermal reactions change in type with temperature, and in extent with time. If the feed-rate decreases, the temperature within the cracking coil rises, and the time of heating lengthens. The optimum combination of temperature and feed-rate must be determined by experiment for each raw-material and apparatus. The raw-materials may be fed to the coils in the form of liquids, or in vapor form as is done by Dr. Alexander. The more accurate the temperature control, the less the formation of carbon.

Two important criticisms can be made of the products made by poorly operated vapor-phase processes, first, the large proportion of olefinic compounds contained, and second, the lack of a proper proportion of the lower boiling hydrocarbons. The "unsaturation" (as determined by the use of concentrated sulfuric acid) of carelessly made vapor-phase gasolines may be as much as 30 per cent to 60 per cent. By proper operation the "unsaturation" can be kept below 25 per cent, and a product made that contains a sufficient quantity of the hydrocarbons boiling below 250° F. The secret of obtaining products of satisfactory quality, with carbon and gas loss of less than 5 per cent, lies in the use of moderate cracking temperature and long reaction time. ᵀᵀ⁻der these same working conditions, carbon difficulties will be found egligible.

ᵔ olefin content of cracked gasoline is not kept within reasonable ifficulty will be had in utilizing the product. The di-olefins, isomers the acetylenes, are the compounds that cause the Fortunately, a gasoline may contain fairly large percentages .ono-olefins and still be used in a motor with satisfaction. :fining should remove the poly-olefins so that no trouble will enced. Figure 102 illustrates the type of difficulty that will ıtered if carelessly made and carelessly refined vapor-phase ;asoline is marketed.

A most important factor in the success of vapor-phase cracking processes lies in the design and firing of the furnace. In my opinion cracking furnaces should be gas fired by means of a number of burners fitted in each combustion chamber. An oil-fired furnace is second

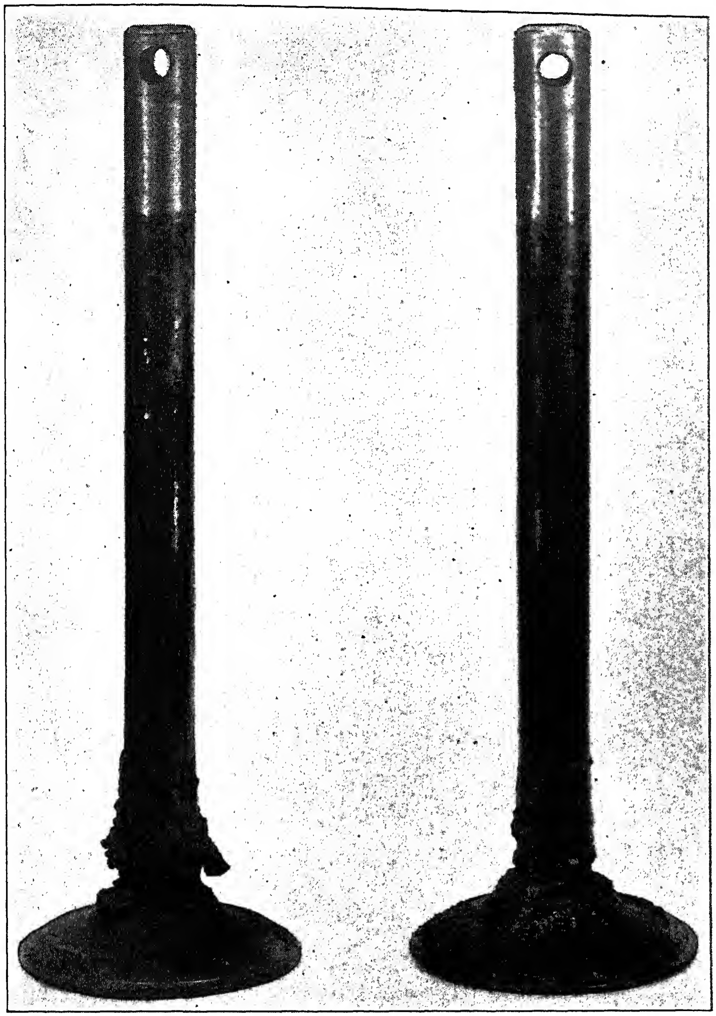


FIG. 102.—Deposit on Valves Caused by Di-Olefins in Gasoline.

choice, and a coal-fired one least desirable. The combustion chamber should be of ample size, and should preferably be located above the coil-heating chamber. Down-draft firing is not essential, but has proved highly satisfactory.

Some difference of opinion exists as to whether it is beneficial to introduce water, steam, or inert low-molecular weight gas into the cracking-coil along with the oil. There is no doubt but that the hydrocarbons decompose more readily in contact with metallic tube walls

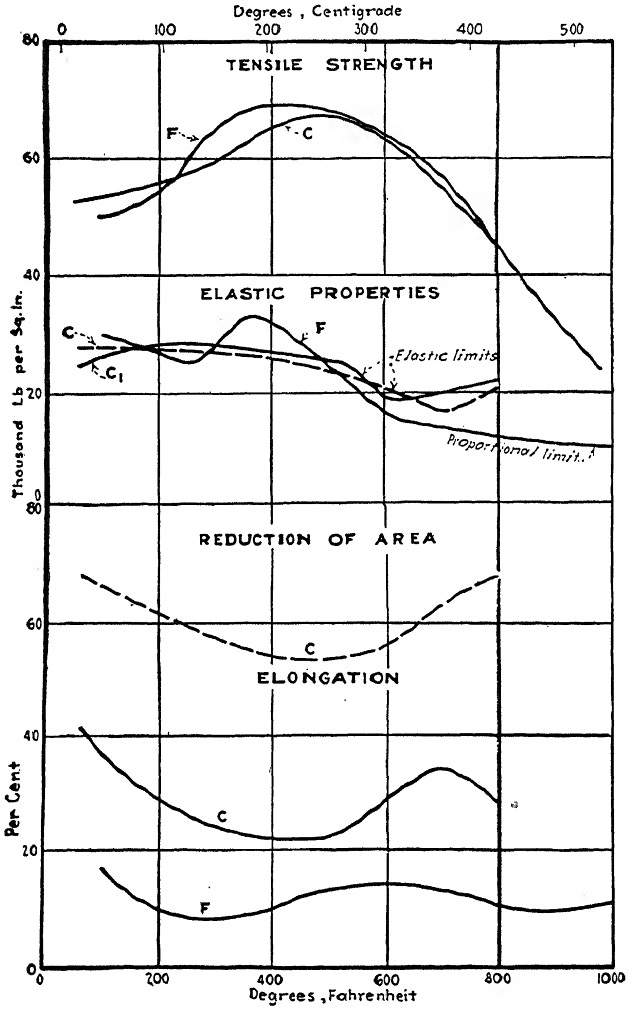


Fig. 103.—Tensile Properties of Wrought Iron and Steel at Various Temperatures.

than when simply heated in space. To conduct heat from the tube-wall to the vapor within, the hydrocarbon molecules composing the vapor must contact with the tube-wall. Opportunity is thereby given for decomposition. If, on the other hand, small inert molecules, such as

H_2O, N_2 or CH_4, are introduced, they will act as heat carriers. The kinetic energy of these small molecules is increased by contact with the tube-walls, whereupon they dive out again into the vapor stream to give up their newly acquired energy. So far as this part of the process is concerned, the use of these heat carriers is beneficial.

However, each of the small molecules occupies space. The volume of the reaction mixture is thus increased, and hence the time of reaction decreased. It is entirely possible that the combination of the longer time of reaction (possible if these gases are not used) and lower temperature would in many instances produce results as good or better than those obtainable with the use of an inert heat-carrier. I am reasonably certain that steam does not have any of the direct hydrogenating effects sometimes ascribed to it. Water vapor does not dissociate appreciably below 3600° F.[6] If the inert vapors are used they must be fed to the cracking tubes with the same accuracy as the oil.

Carbon deposition is frequently mentioned as one of the serious drawbacks to vapor-phase cracking methods. This is nonsense, for it is entirely possible to operate a vapor-phase cracking plant without serious difficulty from carbon. Cracking temperatures below 575° C., and uniform operating conditions are necessary. Working temperatures approaching 500° C. should be the objective of the designer and operator of a vapor-phase cracking plant, and the variation in temperature of the gases leaving the cracking-coil should not exceed ± 5° C.

A simple means of handling the vapors as they exit from the cracking coils is to introduce them on the inner periphery, and at right angles to the axis, of a cylindrical steel chamber. The scrubbing action causes the tar and carbon to build up in stratified layers within the drum. Vapor leaves the drum through openings provided at the end, and on the axis of the drum. The deposited carbon is removed occasionally through a manhead on each end of the drum.

In the design of all heated parts of cracking plant equipment allowance should be made for the lowered tensile strength of steel at elevated temperatures. A recent valuable article by H. J. French,[7] of the U. S. Bureau of Standards, reviews this important subject, and also records the results of recent work done by this author.

Figure 103 shows the results obtained by Huntington, and by Epps and Jones.

The steels tested by French were as follows:

Series	Grade	Specified Tensile Strength 16 per Sq. In.	Composition—Per Cent			
			C	M	P	S
1....	A.S. T.M. Fire-box Spec. A. 30-18	52-62,000	0.19	0.43	0.020	0.031
2....	Marine	60-70,000	0.25	0.38	0.019	0.031
3....	Railway Fire-box	45-55,000	0.17	0.36	0.024	0.031
4....	Railway Fire-box	45-55,000	0.18	0.43	0.017	0.035

[6] Haber, "Thermodynamics of Technical Gas Reactions," pp. 176-7.
[7] *Chem. Met. Eng.*, 26 (1922), 1207-9.

The samples were received as ½-in. plates. All were open-hearth products, during the manufacture of which the baths were kept boiling up to the moment of casting. Such metal is frequently called "open steel."

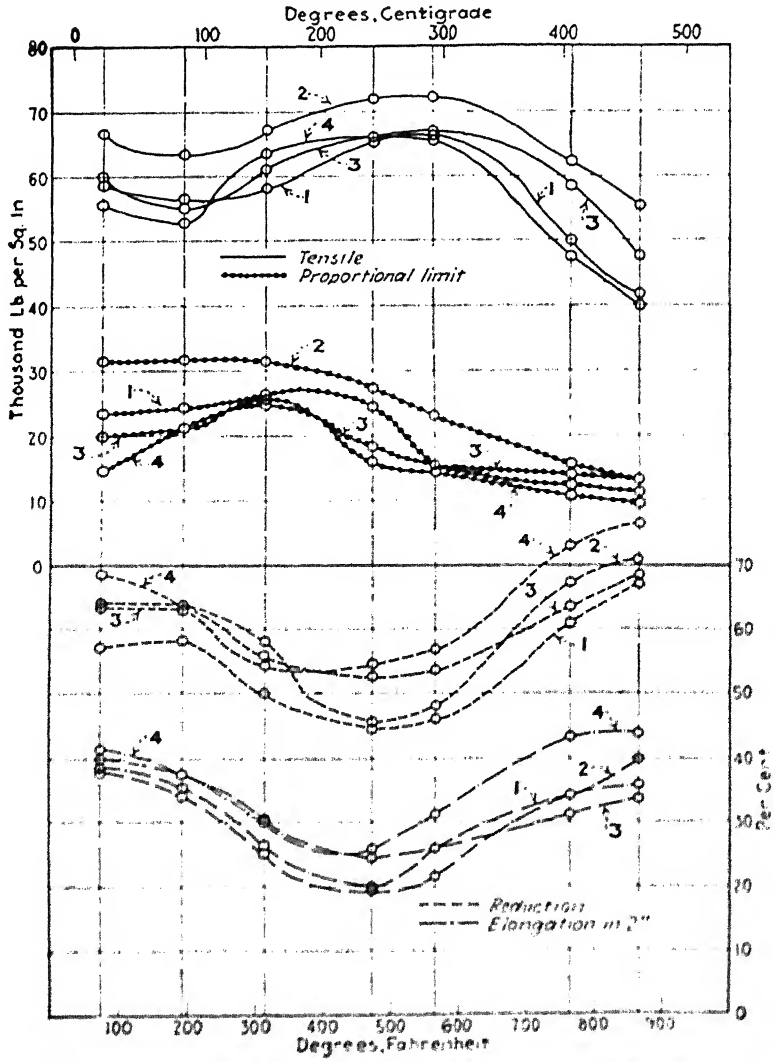


FIG. 104.—Tensile Properties of Four Grades of Boiler Plate Made of Open-Hearth Steel.

For detail of the methods of preparing the specimens and making the tests the reader must refer to the original article. The results of French's tests are shown graphically in Figure 104.

In the design and operation of cracking coils and accessory apparatus that is exposed to temperatures of 400 to 600° C. another peculiarity of low-carbon steel must be taken into account. I have observed, and am confirmed in this by Dr. Greenstreet and others, that after a year or more of service, the metal of the cracking tubes becomes coarsely crystalline and very brittle. Possibly, this is the same phenomenon that is sometimes referred to as Stead's brittleness, although it is my understanding that this latter brittleness develops only when very low-carbon steel is heated for long periods between 650 to 750° C. Much has been written, but little seems to be known of crystallization at low temperatures. The trouble can probably be avoided by the use of tubes made from steel of over 0.2 per cent carbon content. Also, it is important that none of the tubes of the coil, or plates of other apparatus, shall be under severe stress while in service. The whole subject is one that deserves careful investigation.

The design of all apparatus is conditioned by the working pressure used in the process. This brings up the subject of the effect of pressure in vapor-phase cracking. While it must be admitted that high pressures would have a profound influence on the hydrocarbon reactions in the vapor state, it is doubtful if pressures of 75 to 150 pounds have a sufficient influence on the course of the chemical changes to justify their use. Pressure indirectly changes the time of heating, and most discussions of the effect of pressure have failed to distinguish between the effect of pressure as such and the indirect effects of pressure on other variables. A desired reaction time can be obtained in an apparatus of moderate size if pressure is used to pack more molecules into the reaction space. Entirely successful results have been obtained commercially without the use of pressure by Dr. Alexander.

The effect of varying operating conditions is the subject of a recent Technical Paper (No. 258) by E. W. Dean and W. A. Jacobs of the U. S. Bureau of Mines. I wish to point out, however, that it is highly unsafe to draw conclusions regarding vapor-phase cracking from laboratory experiments, and I am unable to concur in several of the conclusions drawn in this paper. It is a common error to attribute to surface catalysis results that are properly ascribable to some peculiarity of heat transfer in the particular apparatus. In so saying, I do not wish to be interpreted as belittling the effects of contact surfaces.

A point that is sometimes slighted in the design and operation of cracking plants is the selection and use of recording instruments for the measurement of temperature. The best instruments should be purchased, and a great deal of care given to installing them properly. Accurate control of all conditions is the price of success in vapor-phase cracking. The quantity and composition of the gas evolved during cracking is often a useful check on operations.

The vapor-phase processes of Greenstreet, Rittman, Alexander, General Petroleum Corporation, Hall, Parker, Texas Oil Products Company, and Ramage are described in the paragraphs that follow.

The Greenstreet Process.

This process was invented by Dr. Charles J. Greenstreet.[8] It is now in use by the Consolidated Oil Refining Company with two plants at E. St. Louis and one at Cleveland, Okla., the Paragon Refining Company of Toledo, Ohio, the British-American Oil Company at Toronto, Canada, the Interocean Refining Company of So. Baltimore, Md., the Pennsylvania-American Refining Co. of Oil City, Penn., and the Gasoline Corporation at East Chicago, Indiana, and Sarpy, Louisiana.

Dr. Greenstreet was a pioneer in the field of vapor-phase cracking, and much credit is due him for his contributions to the art. Application for his first patent was filed in 1911, but his work in this general field dates back to 1908. So far as I am aware, Dr. Greenstreet was the first to gather together such information as was available on the thermal decomposition of hydrocarbons, to add to this from his own experience, and to crystallize the whole in the shape of a process that has stood the test of continued commercial use in the production of gasoline from heavier distillates. He did not choose to discuss his achievements in the technical journals, but this detracts in no way from his accomplishments. The first semi-commercial Greenstreet plant was erected at Cleveland, Oklahoma.

In the Greenstreet plants as operated at present, the oil to be cracked is pumped through feed-valves and meters to the cracking-coil where it mingles with a regulated quantity of steam. The cracking-coil consists of twenty 19- to 20-foot lengths of 2-inch drawn steel tubes placed one above the other, connected into a continuous coil by cast-steel return-bends welded on, and held in place by cast-iron supports. The length of the coil is about 425 feet. The coil-supports are so designed as to allow some movement and adjustment of the coils with stresses. Each coil is supported from an I-beam above the furnace, and can be removed for repair by means of chain blocks.

One type of cracking furnace used by Dr. Greenstreet is fired with coal on a chain-grate. An ample combustion chamber is provided. The hot gases pass upward heating the cracking coils. After passing over the coils, the flue-gas is led inward through ports in the fire-brick dividing wall to a central chamber, and thence downward to the stack-flue below grade.

The furnace consists of two coil-heating chambers with a middle down-draft chamber. The flow of vapor in the cracking coils is counter-current to the flue-gases, that is, the hottest flue-gas heats the tube from which the cracked oil-vapor is leaving the furnace. The walls of the furnace are built of common brick, and lined with firebrick. The entire furnace is properly held together with buck-stays and tie-rods.

The construction of the furnace and the lay-out of accessory appa-

[8] U. S. Patents: 1,110,923, Sept. 15, 1914, "Process of Treating Heavy Hydrocarbon Oils." 1,110,924, Sept. 15, 1914, "Process of Treating Heavy Hydrocarbon Oils." 1,110,925, Sept. 15, 1914, "Process of Manufacturing Olefins and Their Oxidation Products." 1,166,982, Jan. 4, 1916, "Apparatus for Treating Oils." 1,299,172, Apr. 1, 1919, "Process of Treating Mineral Oils."

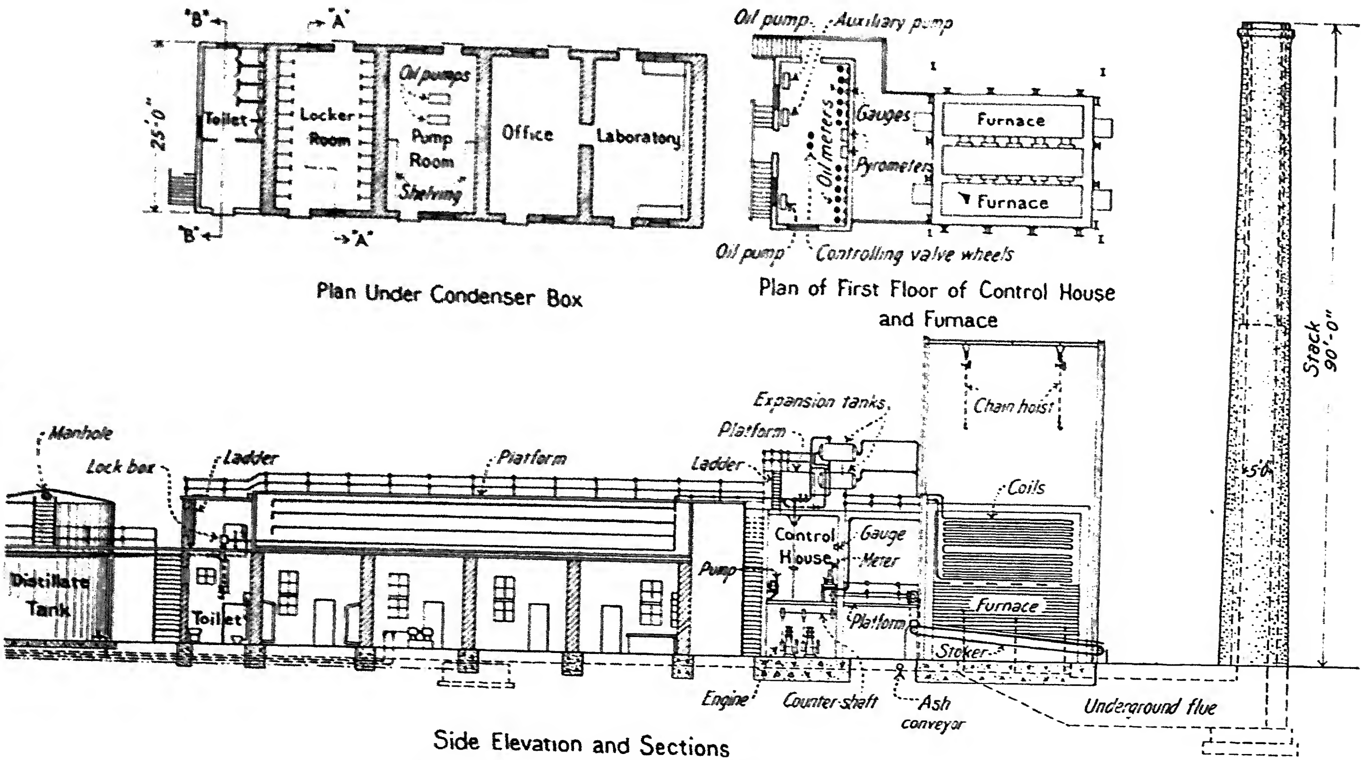


FIG. 105.—Diagram of Greenstreet Cracking Plant.

ratus will be made apparent by an inspection of Figures 105 and 106.[9]

On leaving the cracking-coil, the hot vapor mixture from each coil is led to an individual "expansion" tank or drum. These are seen above the control-house in Figure 106. No expansion takes place here, but the velocity of the vapor decreases, and there is some scrubbing and cooling action, and consequently, a moderate deposition of tarry matter. The chamber adds an element of elasticity to the system, and allows of better regulation of the pressure than would otherwise be possible. The pressure-reducing valves are placed between the expansion tanks and the condenser. The condenser is either of the tubular type shown in Figure 106, or of the box-type shown in Figures 81 and 105. The capacity of the furnace, with six 425-ft. coils in each of the two coil-heating chambers, is 1500 barrels of gas-oil per day. This is equivalent to about five barrels per coil per hour, or 3.5 gallons per coil per minute.

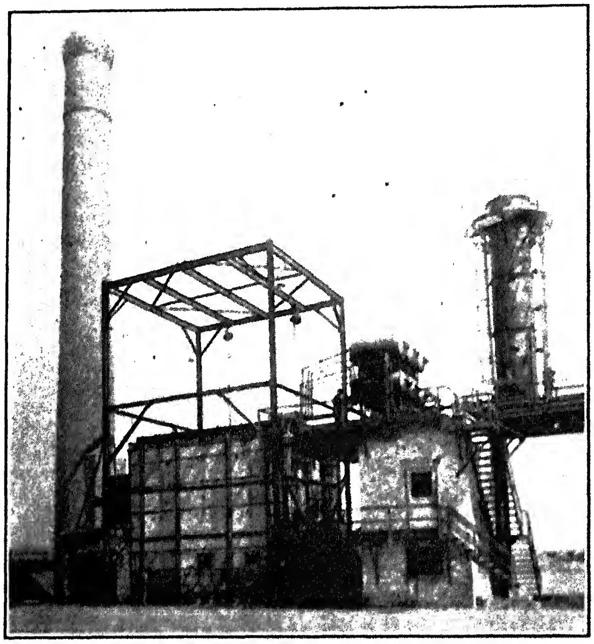


FIG. 106.—Greenstreet Furnace, Expansion Tanks, and Condenser.

The Greenstreet process will successfully handle kerosene, gas-oil and other middle distillates from petroleum. The best conditions for operation must be determined in each instance. The temperature of the hot vapors leaving the furnace is between 900° F. and 1200° F., the pressure used is between 75 lbs. and 150 lbs., and the quantity of steam between 1/8 and 1/3 of the weight of oil treated. The gasoline yield will not be the same for all raw materials, but in a single passage through the cracking coils 25 to 40 per cent of the heavy oil should be converted into a gasoline stock of 450° F. end-point. If the

[9] The originals of these were given to me by Dr. Greenstreet at my request. The information concerning this process has been drawn from an article by R. H. Kinnear (*Pet. Age*, 6 [1919], 76-8), from conversation with Dr. Greenstreet, and from my own experience. The interpretation is entirely my own.

"synthetic-crude" is distilled, and the heavier portions re-cracked, it is possible to produce a total quantity of gasoline equal to 50 to 60 per cent of the volume of the original raw-material. Mr. Schorman,[10] manager of the British-American Oil Company, states that he obtains 36 per cent of 51° Bé. naphtha, and 46 per cent of intermediate distillate, in one passage of the raw material through the furnace. On re-cracking, the intermediate cut 44 per cent of this is obtained as 51° Bé. naphtha. All in all, about 60 per cent of 52 to 54° Bé. water-white gasoline can be made.

Carbon troubles are not a serious factor in the operation of the process. In the early days, the coils were purged with steam twice each day, and then blown with compressed air. The carbon was thus burned out. The blowing must be carefully done as a too vigorous combustion within the cracking-tube will furnish enough heat to melt the metal. Furthermore, oxidation of the inside of the pipe is too rapid if the temperature is allowed to rise excessively during the blowing. At the present time, the properly operated Greenstreet furnace is "blown-down" with air once a week.

The Rittman Process.

The Rittman process has received more popular attention than any other cracking process. This very fact did much to make many refiners suspicious of the merits of the process, and caused ill-founded prejudices that proved a serious obstacle to the general use of the process. Unlike many other processes for which extravagant claims have been made, the Rittman process was conceived by a man who is a sound technologist, and who understands the possibilities in thermally treating hydrocarbons as few understand them. Dr. Rittman would have been the last to have wished the commercial development of his process to savor of politics and extravagant publicity. His attitude in the matter is illustrated by his retort to a gentleman in Washington who took occasion to point out that the publicity his process had received had made him famous. Rittman's reply was, "Like hell it has, it has made me notorious."

Since I am familiar with the early history of the Rittman process, and because the process has not received its fair measure of recognition from the industry, a few comments are in order. The work on which the process was based was done by Rittman in partial fulfillment of the requirements for the Doctor's degree, and in collaboration with Dr. M. C. Whitaker, then head of the department of chemical engineering at Columbia University. Upon receipt of his Doctor's degree, Rittman took employment as a chemical engineer on the staff of the U. S. Bureau of Mines. In a very short time, and undoubtedly without sufficient further experimentation, to say nothing of lack of large scale operation over a reasonable period of time, Rittman's doctorate work was heralded

[10] *Oil and Gas J.*, Nov. 8, 1917, 46.

as a process that could be expected to revolutionize gasoline manufacture as well as benzene and toluene production.

The first application of the process was in the manufacture of

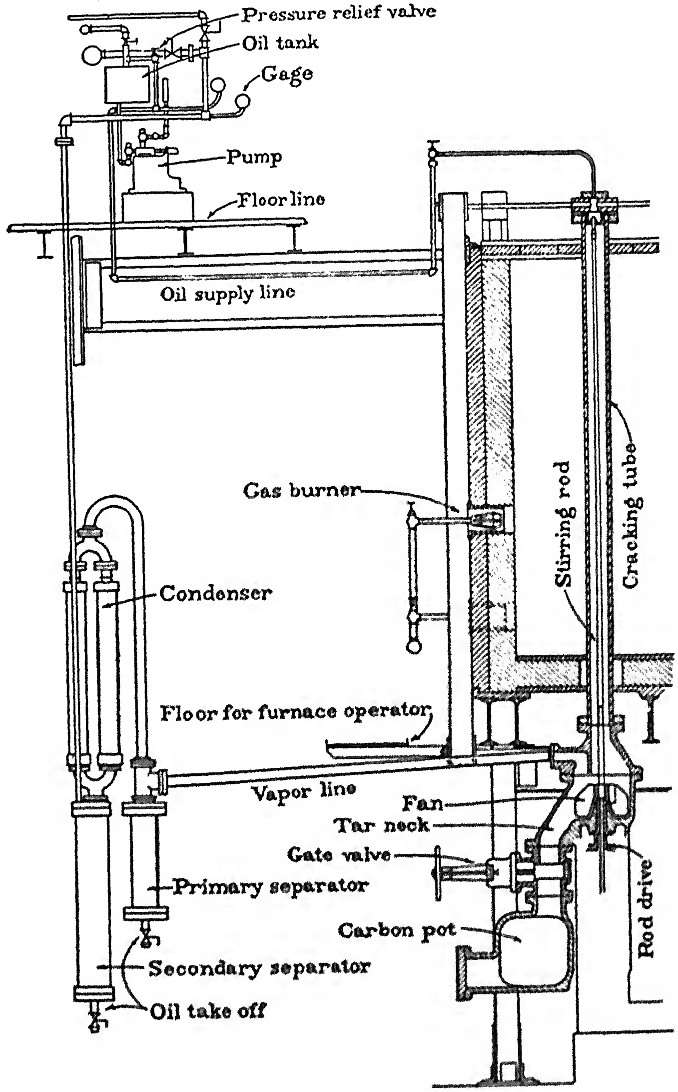


FIG. 107.—Diagram of Rittman's Apparatus.

benzene, a much more difficult task than making gasoline. ...gether with the first several Rittman plants that were built ...oline should properly be regarded as steps in the develop-

ment of the engineering of the process. The cracking processes that are now recognized as successful are the outcome of a long period of experiment and progressive change and development. Rittman was not so fortunate as to be backed by thousands or millions of dollars, and to have every opportunity to develop and standardize his process.

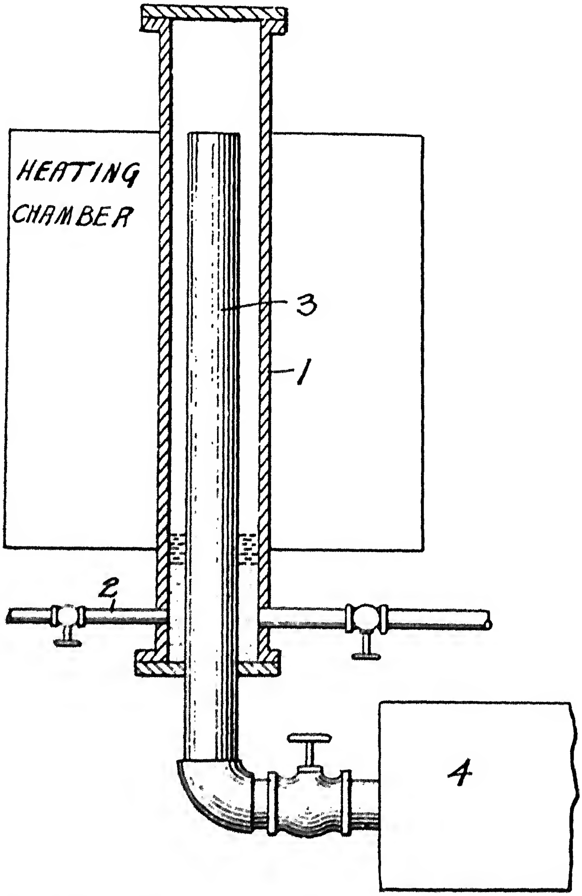


FIG. 108.—Diagram of Later Form of Rittman Cracking Tube.

The thing that strikes me as most remarkable about the Rittman process is the measure of success obtained in spite of premature exploitation not under Rittman's control. Dr. Rittman's contribution to the progress of refinery engineering is not limited to his process, but also includes the publication [11] of the results of valuable investigational work. His thorough knowledge of hydrocarbon chemistry, combined with an extended engineering experience, marks him as a foremost expert in this field.

The Rittman process consists in preheating the heavy distillate, vaporizing it, passing it through a steel tube at a temperature of 500° C. to 575° C. and pressure of 100 to 150 lbs., and then condensing the

[11] *J. Ind. Eng. Chem.*, 6 (1914), 383-92, 472-9. (Published jointly with Dr. M. C. Whitaker.) *J. Soc. Chem. Ind.*, 33 (1914), 626-8. *Bull. 114*, U. S. Bur. of Min., "Manufacture of Gasoline, and Benzene-Toluene from Petroleum and Other Hydrocarbons." (Published jointly with C. B. Dutton and E. W. Dean.) *J. Ind. Eng. Chem.*, 7 (1915), 481-84, 578-82, 945-53, 1019-24, 8 (1916), 20-22.

vapors under the same pressure. As in all vapor-phase methods temperature, pressure, and rate of feed are varied until the best combination for handling the particular raw material is found. The early form of apparatus used is shown in Figure 107.[12] The tubes used were either seamless or lap-welded, 12-in. to 16-in. diameter, 12 ft. to 14 ft. long, walls about 1 in. thick. The fittings were cast-steel. The stirring rod carried a vertical row of 1-in. chains each 10 in. long. A cast-iron paddle was fastened to the bottom of the rod. The chains knocked the carbon off the walls of the cracking tube, and the paddle helped to move carbon and tar toward the carbon-pot. The preheated oil was aspirated into the top of the tube where it vaporized and cracked. The furnace was preferably fired with gas.

A later type of apparatus is shown diagrammatically in Figure 108, taken from U. S. Patent 1,352,916. The oil enters through pipe "2," and fills the cracking tube "1" to such a height that vaporization is as rapid as desired. The vapors are cracked as they pass through the annular space between the inside of the cracking tube and the exterior of the outlet pipe "3." The products pass through pipe "3" to condenser "4." This apparatus presents the distinct advantage of simplicity and of carrying on the reactions in an annular space that can be evenly heated.

A typical Rittman plant is that at Oil City, Pennsylvania, built in 1916. The capacity is 1000 barrels per day, yield 26 to 28 per cent gasoline, and loss about 5 per cent in form of gas and carbon. The capacity per tube is 180 gallons per hour.

Basic patents covering the Rittman process have not issued as yet in this country, but have issued in England. Patents covering a number of features of the apparatus have been granted by the U. S. Patent Office. A list[13] of the patents is given herewith.

For a detailed discussion of the theory and details of this process, the reader is referred to Dr. Rittman's publications, and also to Technical Paper No. 161 of the U. S. Bureau of Mines entitled, "Construction and Operation of a Single-Tube Cracking Furnace for Making Gasoline," by C. P. Bowie. F. L. Slocum and C. C. Stutz have patented[14] improved stirring-rod connections and tar pots.

In the later Rittman plants the size of the tubes has been 8 to 12 in. and the length 11 to 12 ft.

The following is a partial list of the Rittman plants that have been built:

[12] *Bull. 114*, U. S. Bur. of Min., 170.

[13] U. S. Patents: 1,329,852, Feb. 3, 1919, "Carbon-Removing Means." 1,329,-853, Feb. 3, 1920, "Manufacture of Gas." 1,330,008, Feb. 3, 1920, "Treatment of Hydrocarbons." 1,352,916, Sept. 14, 1920, "Apparatus for Treatment of Hydrocarbons." 1,352,917, Sept. 14, 1920, "Apparatus for Treatment of Hydrocarbons." 1,365,602, Jan. 11, 1921, "Treatment of Hydrocarbons." British Patents: 9,162, June 22, 1915. 9,163, June 22, 1915.

[14] U. S. Pat.: 1,304,211, May 20, 1919. 1,304,212, May 20, 1919.

Island Refinery Co., Pittsburgh, Pa.
Germania Refining Co. Oil City, Pa.
Gulf Refining Co., Port Arthur, Tex.
Indian Refining Co., Lawrenceville, Ill.
Empire Refining Co., Okmulgee, Okla.
Midwest Refining Co., Casper, Wyo. (This plant was under the supervision of Dr. David T. Day.)

So far as I am aware, the Rittman process is not being pushed today, mainly because of lack of a promoter. It is a good example of the stagnation that results when a process is free for all.

Alexander Process.

A highly successful vapor-phase cracking plant was designed and built for the Gulf Refining Company at their Port Arthur, Texas, plant by Dr. Clive M. Alexander, then in charge of refinery development work for this corporation. This cracking plant had a maximum capacity of 10,000 barrels of gas-oil or kerosene per day of 24 hours. Over a period of time the operating capacity was 8,000 barrels daily. The cost of the complete plant was about $1,250,000. During the year 1918 the raw material used was a mixture of 50 per cent gas-oil and 50 per cent kerosene distillate, and the average yield of gasoline was 27.6 per cent. This gasoline had a gravity of 52 to 54° Bé., initial boiling point of 130 to 140° F., end point of 420 to 430° F. and otherwise met the Government standard specifications.

The plant consisted of five divisions, and each division of four benches of vertically-set cracking tubes. The tubes were 6 in. in diameter and almost 20 ft. long. The oil was first vaporized in pipe-stills, and the vapor at a temperature of 600 to 700° F. was distributed to manifold pipes from which it flowed through properly sized orifices to the cracking tubes. These were maintained at a temperature of 900 to 1000° F. No pressure was used. The hourly capacity of each tube was 20 to 25 gallons of heavy distillate.

The vapors from the cracking tubes were passed through a series of towers and heat exchangers in order to fractionate them and to conserve heat. The yellow crude cracked naphtha obtained in this manner was refined with sulfuric acid and caustic soda in a continuous treating plant, and then re-run with steam, whereupon a water-white gasoline was obtained. No difficulty was encountered with the product going off color either in storage or in shipment.

A panoramic view of this plant is shown in Figure 109. The power plant is seen at the extreme left, the furnace building in the center, and the refining and re-running equipment at the right. An operating force of one hundred men was required. During 1919 the price of kerosene and gas-oil rose to such figures that operation of the plant was not profitable. It was temporarily used for topping Mexican crude oil. However, whenever the relative prices of gasoline and heavy distillates are such that cracking is profitable, this plant will doubtless

be used for cracking. It has the distinction of being the largest vapor-phase cracking-plant in existence.

I am informed by Dr. Alexander that experiments were tried with 4-in. cracking tubes. These were found to be satisfactory and had an hourly capacity of 15 gallons of 32° Bé. gas-oil when producing 25 per cent of gasoline. Experiments were also tried with a combination of tubes consisting of a 4-,. and 8- and a 14-in. set concentrically and vertically in such a manner that the heavy-oil vapors entered the 4-in. pipe, travelled through it into the annular space between the 4-in. and 8-in. pipes, and thence into the annular space between the 8-in. and 14-in. pipes. The vapor was preheated during its passage through the 4-in. pipe and the first annular space, and cracked during its passage through the outer annular space. The capacity of such a cracking tube combination was 60 gallons per hour of 32° Bé. gas-oil.

The process of Alexander is covered by the U. S. patents here listed.[15]

General Petroleum Corporation Process.

In 1916 the General Petroleum Corporation of Los Angeles, California, purchased the Western rights to a vapor-phase cracking process controlled by the New Process Oil Company of St. Louis by virtue of its ownership of the patent [16] of C. H. Washburn. Mr. Washburn had been previously employed by Dr. Greenstreet, and there is a striking similarity between Washburn's method as described in his patent and that of Greenstreet.

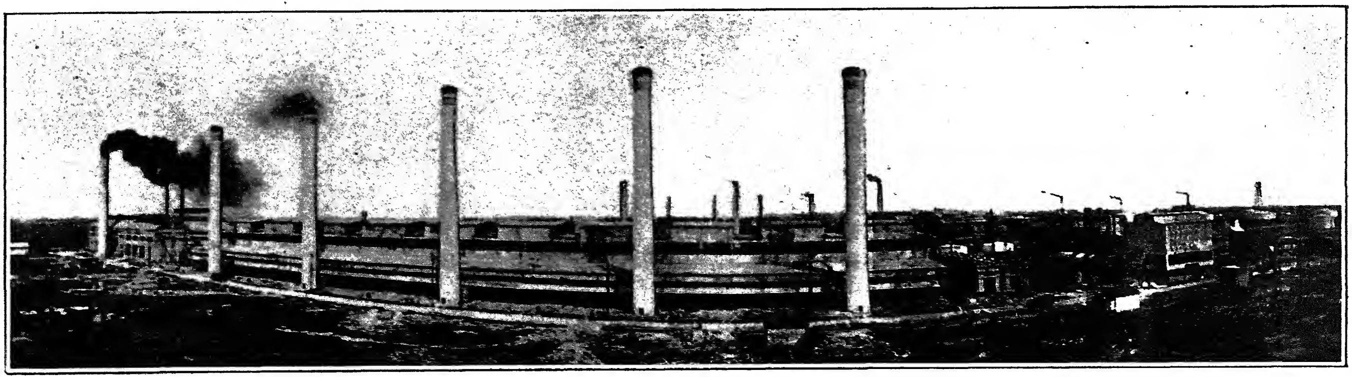
The process as first used by the General Petroleum Corporation was unsuccessful both from the standpoint of yield and quality of product. The difficulty lay partly in the design of the furnace, but largely in the use of wrong working conditions, and in careless control. The writer, then in the employ of the General Petroleum Corporation, took the process in hand, and with the help of Mr. Tunison and Mr. Barbre of the research laboratory and Mr. Fred Isaacs, operating superintendent, placed the plant on a profitable working basis.

Distillate of 38° Bé. and water were fed to the cracking coils in the proportion of one volume of oil to ⅛ volume of water. The temperature of the vapor mixture leaving the cracking coils was 575° C. The vapor was condensed under 75 to 80 lbs. pressure. The yield of gasoline of 437° F. end point approximated 40 per cent.

A general view of part of the first plant is shown in Figure 110. Two cracking furnaces, each of 400 barrels daily capacity are shown at the left to the rear, the continuous pipe-still for re-running in the center, part of the steam-still equipment at the right, and a few of the run-down tanks in the foreground. The cost (1916-1917) of the plant, including cracking furnaces, re-run pipe-still, steam-stills, agitator,

[15] U. S. Patents: 1,387,677, Aug. 16, 1921, "Process of Heating Oil-Retorts and Apparatus Therefor." 1,404,725, Jan. 31, 1922, "Process of Making Low-Boiling Hydrocarbons." 1,407,619, Feb. 21, 1922, "Manufacture of Motor-Fuel."

[16] U. S. Patent: 1,138,266, "Process of Treating Hydrocarbon Oils."



Courtesy of C. M. Alexander.

FIG. 109.—Alexander Cracking Plant of the Gulf Refining Company.

tanks, pump-house, and all accessory equipment, was less than $150,000. The capacity could have been trebled for an additional investment of $75,000. Just at the time that further cracking furnaces would have been built, the demand came for toluene, and this plant was made the nucleus of the toluene-plant briefly discussed below.

The cracking coils in the gasoline plant were made of 2-in. extra-heavy mild steel pipe, and connected by return-bends into a continuous

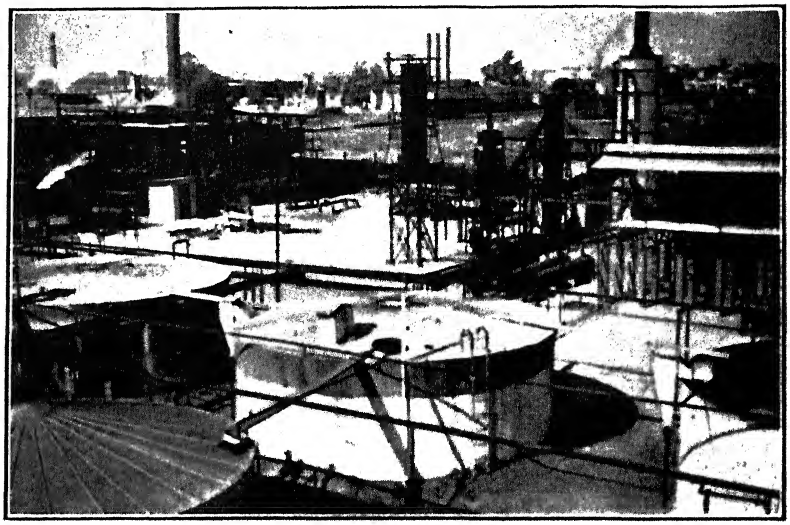


FIG. 110.—First Units of the New Process Plant of the General Petroleum Corporation.

coil 250 feet in length. One furnace contained eight coils and the other nine. The fuel consumption was equivalent to 2.8 per cent of the distillate run through the coils. Loss in the form of gas and carbon was equivalent to 5.0 per cent of the distillate run, and all losses in re-running, refining, and steam-stilling were equivalent to 2.5 per cent of the raw material. The following analysis is typical of those of the gas formed:

	Per Cent
Methane	57
Ethane	10
Ethylene	16
Hydrogen	15
Other	2
Total	100

The Manufacture of Toluene from Petroleum.

The manufacture of the aromatic hydrocarbons from petroleum distillates is so closely connected with the production of gasoline that I

cannot refrain from briefly describing the methods used at the plant of the General Petroleum Corporation. Shortly after my connection with this corporation in 1916, I started experimental work to determine what yields of toluene could be made from California distillates. It appeared that they should be ideal raw materials on account of their cyclic structure. The experimental work was highly successful.

Early in 1917 samples were sent to the DuPont Company, and also to other manufacturers. Shortly after this, Mr. Yerkes and Mr. Marshall of the DuPont Company paid a visit to the plant. The result of this was that eight months after the United States had entered the war a group of engineers headed by Mr. Dickey of the United Gas Improvement Company was sent by the Government to look over the toluene plant and process. They were given the fullest information together with numerous suggestions in the way of mechanical improvements. The result of all this was that a large plant was built at the refinery of the General Petroleum Corporation at Los Angeles and another at the plant of the Standard Oil of California at Richmond, California.

The following quotations are taken from pages 106 and 108 of "America's Munitions" by Benedict Crowell, Director of Munitions and Assistant Secretary of War.

"How to increase the supply of toluol, the basic raw material from which T.N.T. is made, was the greatest and most pressing of all the problems in regard to the existing raw materials.

"Three general sources existed from which toluol was obtained: first, from the by-product recovery coke-ovens; second, by the stripping or absorbing of toluol from carbureted water-gas and coal-gas; and third, by the cracking or breaking down of oils.

"For the production of toluol by cracking crude oils or petroleum distillates, three processes of the many submitted were officially approved and contracts awarded for operation.

"The first and most important of these was that of the General Petroleum Corporation of Los Angeles, California. Under their scheme a yield of 6 per cent toluol was obtained from a petroleum distillate, of which there was a large quantity available, by treatment under temperature and pressure. To facilitate production of toluol by this means, two large plants, one at Los Angeles and the other at San Francisco, were erected at a cost of approximately $5,000,000. These plants have a monthly capacity of 3,000,000 lbs. of toluol and their construction destroyed all possibility of a shortage in this vital raw material.

"Another process was that known as the Rittman process, evolved by a scientist of the Bureau of Mines. This scheme, which called for producing toluol from solvent naphtha or light oils by cracking under high pressure and temperature, was finally demonstrated to be capable of operation under war conditions, and production had just started at a plant at Neville Island, Pittsburgh, Pa., at the time of the signing of the armistice.

"A third process was that known as the Hall process, by which

toluol was also obtained by cracking solvent naphtha under high pressure and temperature by another, different, mechanical system. This scheme was in operation on a small scale during 1918 at the Standard Oil Plant, Bayonne, N. J."

I feel that the above quotations do not give Dr. Rittman the credit that he deserves in connection with the manufacture of synthetic toluene. It was his work at Columbia University in 1913-14 and later with the U. S. Bureau of Mines that woke us up to the possibilities of producing aromatic hydrocarbons by thermally treating petroleum oils or coal-tar distillates.

In running through the pages of a recent number [17] of the *Journal of Industrial and Engineering Chemistry*, I was interested to note a statement made by H. S. Miner in the course of his address of presentation of the Grasselli medal to Mr. Walter H. Fulweiler in recognition of his paper, "Chemical Problems of the Gas Industry." In recounting Mr. Fulweiler's accomplishments, he says, "Like many another loyal chemist connected with our 'key' industries, he collaborated with the Ordnance Department during the war, studying particularly the manufacture of toluene. In addition to reporting on several methods for the production of this material so urgently needed at this time, he developed and perfected a process for its manufacture by a heat treatment of California distillates, and assisted in the construction and operation of two plants embodying this process,—one at Los Angeles and the other at San Francisco, the former having a production of three million gallons a year at the time of the armistice."

The plant referred to in this statement is that of the General Petroleum Corporation, and the substance of this statement is wholly unwarranted in so far as the development of the process is concerned. If ideas on toluene manufacture in this country are traced back to headquarters, it will be found that they emanated from Dr. Whitaker's graduate laboratory at Columbia University, and that Rittman's Doctorate work was the first important piece of research in this general field.

My own interest in this subject was aroused at Columbia, and it was only natural that later, when in charge of development work at the refinery of the General Petroleum Corporation, I should have put theory into practice. The toluene process of the General Petroleum Corporation was developed by the organization of which I was in charge when employed by this Corporation. Mr. B. R. Tunison and Mr. Clarence Barbre assisted me in this work, and deserve no small measure of the credit for the development of the process. Mr. Dickey and other engineers, and later Mr. Fulweiler, sent to Los Angeles by the Ordnance Department, came to see a working process, and not a laboratory tube-furnace. They were given the benefit of plant practice then existent, and in addition the combined ideas and suggestions of the technical organization of the General Petroleum Corporation. The services of these gentlemen were of real value in the construction of

[17] *J. Ind. Eng. Chem.*, 14 (1922), 1154-5.

the Government plants, with which I had nothing to do because of the necessity of my presence in the East in connection with other important war work. However, the statement I have quoted above, in regard to the conception and development of the process, is rather too badly in error to pass uncorrected by me.

The Hall Process.

The Hall process is the invention of William A. Hall, and is covered by several[18] U. S. Patents. In an address[19] before the Institution of Petroleum Technologists in London on February 18, 1918, Hall described his process as follows:

"The oil is fed at a rate exceeding 70 gallons per hour through inch tubes of more than 300 foot length, under 50 to 75 lbs. pressure, and so throttled that the speed of the vapor through the tubes exceeds 5,000 feet per minute. The oil is first vaporized in a coil, preheated in the flue by the waste heat of the products of combustion from the furnace, so that it enters the cracking tubes at a high rate of speed. The speed is so great that very little deposit can be formed in these tubes to choke them and interfere with the cracking action, but, as the passage of the vapors through the tubes occupies only about three seconds, no very extensive cracking occurs, as is proven by samples extracted at these points. The temperature read on a pyrometer, its thermal couple being located in the center of the tubular nest, is about 550° C.

"The vapors issuing pass into a vertical pipe of twelve or more inches internal diameter and about 12 feet high, entering it through a very confined space acting as a throttle, and preferably impinging against a baffle in the large pipe, so that the speed of flow is instantly reduced from about 6000 feet per minute to a very nominal rate. This converts the energy of speed into that of heat, a sort of degrading action, much the same as takes place in a throttling calorimeter, the temperature actually increasing some 30° C., notwithstanding the expansion due to a reduction of pressure from 50 pounds or 70 pounds to about atmospheric. Hence we have in this large pipe, which is well insulated, a temperature well above that existing in the inch tubes of the cracker, and as the speed through this large pipe is comparatively slow, a large amount of cracking therein takes place with no extraneous application of heat, affording no chance for a superheating of the vapors to a temperature higher than that at which cracking takes place.

[18] U. S. Patents: 1,105,772, Aug. 4, 1914, "Process of Making Gas from Oil." 1,175,909, Mar. 14, 1916, "Process for the Conversion of Heavy Hydrocarbons into Lighter Hydrocarbons." 1,175,910, Mar. 14, 1916, "Process of Making Motor Fuel." 1,194,289, Aug. 8, 1916, "Process of Cracking Hydrocarbons." 1,201,930, Apr. 9, 1917, "Converting Hydrocarbons." 1,239,099, Sept. 4, 1917, "Hydrocarbon Product." 1,239,100, Sept. 4, 1917, "Liquid Fuel." 1,242,796, Oct. 9, 1917, "Producing Motor-Fuel." 1,247,671, Nov. 27, 1917, "Distillation of Heavy Oils, Oil Residues, and Bitumens." 1,261,930, April 9, 1918, "Art of Converting Hydrocarbons." 1,285,136, Nov. 19, 1918, "Apparatus for Making Motor Fuel."

[19] *J. Inst. Pet. Tech.*, 1 (1915), 147-66.

"By this method the interior of the mass is hotter than the exterior wall of the container, and all the vapors in their upward passage are working towards a cooler condition, thus preventing local superheating which has always produced the largest amounts of fixed gas from what would otherwise have been condensable product of the character most desired in motor-spirit.

"This pipe is filled with the small pieces of thin tubing before-mentioned, which present an enormous surface to collect all the carbonaceous deposit.

"One might think that this very large chamber, with all its surfaces, and with the slow passage of vapors through it, would act as a dephlegmator rather than a cracker, but in actual practice, even with oils of a gravity exceeding 0.960, and some very high-boiling fractions, no liquid condensate has ever been collected from the bottom, and the higher the rate of feed of oil, at the same temperature in the cracker, the higher is the temperature in this secondary cracker.

"The actual temperature of the vapor in the lower portion of this receptacle may exceed the external temperature of the tube near its exit, but inside the furnace, by about 30° C.

"From this receptacle the vapors pass through dephlegmators that separate all fractions boiling below the chosen point of cut, and the vapors and gases passing on are conducted without further condensation, and at a depression, into a mechanical compressor working under 70 to 100 lb. per sq. in., and then condensed through a cooler under that pressure. The object of the compressor is twofold: Firstly and of least importance, it is a means of drawing these vapors at substantially atmospheric pressure through the secondary cracker and the dephlegmators; and secondly, it is a means of chemically attaching to the condensable liquid the gases that would otherwise be permanent."

With reference to the chemical reaction last referred to Hall says, "That an actual and important chemical reaction does take place, has now, I believe, been established to the satisfaction of some of our best experts."

Hall states that he has tried all pressures from a slight vacuum up to 1500 lbs., but has adopted 50 to 75 lbs. as most practical. At the higher pressures leaks occur, and heavy tubes are necessary. Less fixed gas is evolved, however. He emphasises the importance of accurate temperature control and says, "Supposing the external temperature in the center of the nest (of tubes) is 560° C., a change from 20° C. below that point to 20° C. above may make a difference of 50 per cent in the production of gas, and a great difference in the gravity of a spirit boiling below a given point, but still more marked is the difference in the unsaturated portions. I have seen a spirit produced of 90 per cent unsaturated, and another of only 30 per cent unsaturated, both from the same oil, with the same point of cut and the same pressure, in fact, with all conditions the same except this comparatively small difference in temperature."

Hall claims that an endothermic chemical change occurs in the

compresser that forms part of his apparatus. He says, "If no endothermic reaction took place, the condensation of these vapors and compression of the gases would create an increase of temperature, so the heat absorption of the reaction is sufficient, not only to offset that natural physical increase that would be expected, but to reduce it still further—many tests showing a drop of temperature of fully 30° C. between the inlet and exit of the compressor, and this when operated without water in the jacket, the readings being taken by thermometers placed so their bulbs were as close to the moving piston as practicable." Further details of this most interesting phenomenon are given in his paper.

The results of a demonstration of the Hall process are reported by Dr. Charles F. Chandler.[20] A 44.5° Bé. gas-oil was used as the raw material. The products were 52° Bé. motor-spirit 55.9 per cent, light residue 31.6 per cent and heavy residues 3.4 per cent, carbon and gas 9.1 per cent. The light residuum was re-cracked yielding 45 per cent of its volume as motor-spirit. These experiments were carried out at Greenpoint, L. I., in 1913.

Although Hall is an American, he chose to attempt the first commercial development of his process in England. In this country the Texas Company took the process in hand, and in November, 1916, started a 500 barrel plant in operation. From gas-oil or low grade kerosene distillate a yield of about 40 per cent gasoline is obtained in one passage through the apparatus. The coils in this plant consist of 640 feet of 1-in. cold-drawn steel tubing. Automatic temperature control is used.[21]

I feel that it would be interesting to see Hall's claims in regard to the endothermic chemical changes in the compressor and in regard to the rise in temperature in the auxiliary or secondary cracking chamber confirmed. If one assumes a vapor velocity of 100 feet per second, treatment of 70 gallons of oil per hour, heat capacity of the vapors 0.5 B.t.u. per pound per 1° F., complete conversion of kinetic energy into heat, and no heat losses, the temperature rise in the secondary chamber would be only 7° to 8° C. rather than 30° C. as claimed. Adiabatic pressure increase might add a little more heat, but it should also be kept in mind that the hydrocarbon decompositions and dissociations are endothermic, so the heat causing the temperature rise must be in addition to that absorbed by the reacting system.

It would also appear that cracking in the presence of scrap-iron is essentially wrong, for iron is known to be one of the metals that catalyzes dehydrogenation. A secondary chamber similar to that described in the introduction to my discussion of vapor-phase cracking would handle the carbon and tarry substances effectively, would allow of the secondary cracking, if this in fact occurs, and would avoid dehydrogenation as well as the nuisance of removing and cleaning the scrap-iron filling material.

[20] *J. Ind. Eng. Chem.*, 8 (1916), 73-5.
[21] James, H. G., *Oil and Gas J.*, Nov. 8, 1917, 39.

The Parker Process.

The Parker process[22] consists in passing a distillate which it is desired to crack, through a 150-ft. preheating coil of 1-in. pipe, through a jacketed tube heated by superheated steam to 800 to 900° F., through a cylindrical reaction chamber that contains a metal screw or helix, and finally through an expansion drum to a water-cooled condenser. Steam in an amount equal to about 1/10 of the weight of the oil is injected as the oil and vapor enter the jacketed-tube. The inventor claims that the motion of the vapor in the reaction chamber with the helical baffle is such that the heavier portions of the vapor, that is, the higher molecular weight hydrocarbons, are thrown toward the periphery of the chamber, and that a selective decomposition is thus obtained. The vapor velocity is said to be 100 feet per second.

It is my opinion that the only result of the passage of the vapor through the helically baffled chamber will be a thorough mixing of the vapor. Certainly no separation of gaseous molecules will result from this operation. In this connection, reference should be made to the discussion of the effects of centrifugal force on solutions in Nernst's "Theoretical Chemistry."

Except for a few mechanical details that are apparently of little consequence, the Parker process is essentially the same as that of Greenstreet. Parker was superintendent of the first semi-commercial Greenstreet plant erected at Cleveland, Oklahoma, and later went to Galicia and Roumania to erect Greenstreet furnaces.

I understand that the Parker plants have been none too successful, and in some cases have been complete failures. This has doubtless been the result of lack of careful control, for the same basic principles underlie the Parker process as successful vapor-phase processes.

According to Mr. H. C. James,[23] the Parker apparatus as actually built comprises a furnace about 50 ft. long in which six coils of 2-in. pipe 300 ft. long are heated. The drums, two per furnace, are 2 ft. in diameter, 12 ft. long and fitted with helical steel baffles. A pressure of 60 lbs. and a furnace temperature of 1500° F. are used. A unit having a daily capacity of 400 to 600 barrels of distillate costs about $25,000. When 42° Bé. kerosene is used as raw material, a 42° Bé. synthetic crude is produced that contains 25 per cent of gasoline and 25 per cent kerosene. The heavier portions are cracked again. The gasoline referred to had a gravity of 50.6° Bé. and an end-point of 410° F. By cracking and recracking, an average of 65 per cent of gasoline should be made.

The following is a partial list of Parker plants that have been built:

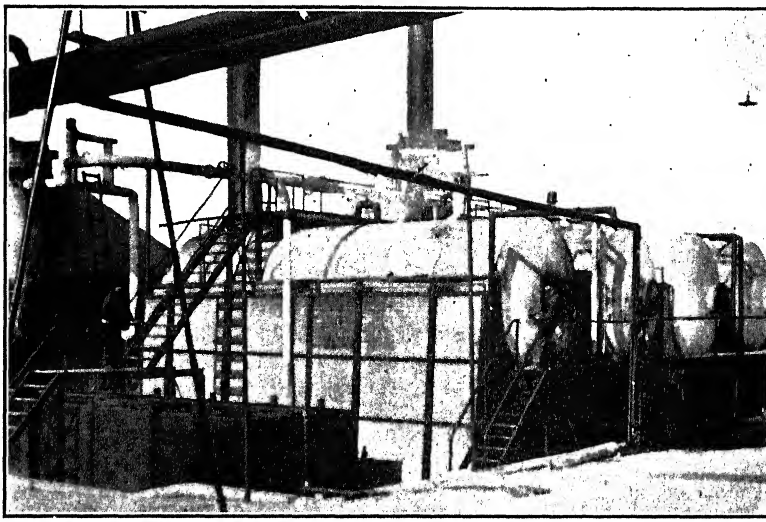
North American Refinery Co.	Pemeta, Okla.	400 Bbl.
[illegible] and Owen	Cushing, Okla.	400 "
[illegible]ocess Refinery Co.	" "	400 "

Pat. 1,226,990, May 22, 1919, "Process for Refining Oils."
Gas J., Nov. 8, 1917, 38-9.

Eagle Refinery Co.	Cushing, Okla.	800	Bbl.
Amos Refinery Co.	" "	400	"
Petroleum Products Co.	" "	400	"
Consumers Oil & Refinery Co.	Yale, Okla.	800	"
Hudson Refinery Company	" "	400	"
Imperial Refinery Co.	Ardmore, Okla.	400	"
Lawton Refinery Co.	Lawton, Okla.	400	"
Nyanza Refinery Co.	New Wilson, Okla.	400	"
Dansinger Bros.	Drumwright, Okla.	800	"
Callahan & Co.	E. St. Louis, Ill.	800	"

The Process of the Texas Oil Products Company.

The Texas Oil Products Company of Waxahachie, Texas, through agreement with the Bostaph Engineering Company of Detroit, Michigan, controls U. S. Patent No. 1,224,787, issued to Dr. A. S. Ramage on May 1, 1917. The patent specification states, "My invention is a process whereby hydrocarbons are transformed, by restricted oxidation



Courtesy of C. M. Alexander.

FIG. 111.—Pressure-Stills Used as Vaporizers by the Texas Oil Products Company.

effected through the agency of a suitable reducible metallic oxide into other hydrocarbons containing proportionately less hydrogen, water being produced in the reaction." Paraffins are supposedly converted into olefins, terpenes, and aromatic hydrocarbons.

This patent is the first that has come to my attention that claimed such a transformation as being at all desirable, and I am inclined to believe that Dr. Ramage has changed his views since the date of issue of this patent.[24]

[24] See description of the Ramage process used by the Barnsdall Corporation.

In a private communication, I have been informed by Dr. C. M. Alexander, manager of refineries of the Texas Oil Products Company, that the process as developed up to the time of the erection of the Waxahachie plant was not commercially successful. Since that time many changes have been made, and the process now used by the Texas Oil Products Company is giving excellent results.

Oil vapors are passed over iron-ore in heated tubes, the iron oxide functioning as a catalyst, but also being reduced in some measure. When the catalyst no longer functions properly the tube is purged with steam, and then blown with air to oxidize that part of the catalytic material reduced during the cracking period. Reduction and oxidation of the catalyst must be skillfully controlled, for otherwise the iron-ore swells and balloon-like bulges are formed along the cracking tubes.

The plant at Waxahachie consists of six converters with fractionating towers and cooling and condensing equipment, four 10 x 30 ft. pressure-stills for vaporizing the distillate at constant and controlled pressure, four 10 x 40 ft. re-run stills with fractionating towers and condensers, gas-scrubbing unit, continuous treating plant, and necessary tanks and pumping equipment. One thousand barrels of crude-oil is handled daily. The products are 650 barrels of gasoline, and 200 barrels of fuel-oil. Fifteen per cent of the original oil is converted into carbon and gas. The fuel-oil produced is sufficient to operate the entire plant. Hence, the two products sold are gasoline and gas. This type of plant practice, that is, conversion of everything into gasoline, fuel-oil, and gas, is interesting in that it is a forerunner of the technology that will be the basis of operations in many future refineries.

The pressure-stills at the plant of the Texas Oil Products Company are shown in Figure 111. These are used to generate vapors that are cracked by the vapor-phase method.

The Ramage Process.

The process of Dr. A. S. Ramage covered by U. S. Patents Nos. 1,403,194 and 1,409,404 is used by the Barnsdall Corporation under an agreement with the Chemical Research Syndicate of Detroit. This process, and that used by the Texas Oil Products Company, are unique in being the only successful processes using catalysts other than aluminum chloride. The patent specification states, "The object of this invention is to form low-boiling hydrocarbons, chiefly of a saturated nature, suitable for use in internal combustion engines, from heavier hydrocarbons such as heavy fuel-oils and crude-oils, and more especially oils of a very heavy asphaltic nature."

Heavy oil vapors mixed with steam are brought into contact with ferrous oxide at temperatures of 550 to 600° C. The proportions of
hydrocarbon vapor are so adjusted, according to the patent,
l material oxidation of the ferrous oxide to ferric oxide on
and material reduction to metallic iron on the other. It
the hydrogen, formed when water is reduced by ferrous

oxide, combines with the unsaturated hydrocarbons to produce saturated hydrocarbons. Much of the oxygen of the steam appears in combination with carbon as carbon monoxide. Reference should be made to the patent for an exposition of the theory of the process.

I am not familiar enough with the engineering details of the Ramage plant of the Barnsdall Corporation to describe its design, but I am informed by Dr. Ramage that the results obtained are highly satisfactory.

LIQUID-PHASE CRACKING PROCESSES.

The liquid-phase processes are at present of far greater commercial importance than the vapor-phase processes. One of the main reasons for this is the better quality of the product, both with respect to boiling range and olefin content. With the exception of the aluminum chloride processes and the process of Leslie and Tunison, all liquid-phase processes use pressure. This is an inherent disadvantage, but by no means an unsurmountable one. However, it limits the usable raw materials to those heavy distillates that do not deposit an excessive amount of carbon during cracking.

The Burton process is by all odds the most important liquid-phase process, although several of the others are attracting attention at this time and may soon be widely used.

In the paragraphs that follow the processes of Burton, Holmes-Manley, Fleming, Cross, Dubbs, S. O. of New Jersey, Emerson, Jenkins, Isom, Bacon-Brooks-Clark, Coast and Cosden, "Coast-Improved," Muehl, G. W. Gray, McAfee, and Leslie-Tunison will be discussed.

The Burton Process.

The process invented by Dr. William M. Burton, and developed by the Standard Oil Company of Indiana, is the most widely used of all cracking processes. Some writers have professed to see little in this process that was not disclosed in the patents of Dewar and Redwood,[25] and less directly in those of C. S. Palmer.[26] Apparently these opinions are concurred in, at least in part, by the Standard Oil Company of Indiana. Mr. Russell Wiles of the firm Dyrenforth, Lee, Chritton and Wiles, attorneys for the Standard Oil Company of Indiana, said at a recent hearing before a special master at Santa Barbara, California, "The Burton process as we use it today is substantially the Dewar and Redwood process, with added improvements we have made ourselves, not having the slightest relation to where the valve is (pressure control valve), or how far the pressure goes. That never was a point of novelty in the Burton process. The Burton process never depended on that in the slightest degree."

However, the patent of Dewar and Redwood covered a process for

[25] U. S. Patents: 419,931, Jan. 21, 1890; 426,173, Apr. 22, 1890. English Patents: 10,277 (1889); 13,016 (1890); 5,971 (1891).

[26] U. S. Patent: 1,187,380, June 13, 1916. Application filed March 2, 1907.

making large yields of burning oils, and it is denied by Redwood [27] that he and Dewar were aiming at the production of "petrol." In fact, they burned this product under the stills. The Palmer patents are now controlled by the Standard Oil of Indiana. Those of Dewar and Redwood long since expired. I am informed by Dr. Greenstreet that he tried pressure-still cracking before the experiments of Dr. Burton were carried out, but abandoned it because of the hazards involved.

Whatever may be the truth as regards the validity of the Burton patents, the fact remains that the development and use of the process is the outstanding feature of petroleum technology in the last decade. Doubtless, the next ten years will see many new and valuable processes developed and used, but the Burton process does not need to look to the future for its laurels. It is a realized and commanding achievement.

Dr. Burton has been the recipient of high honors because of his useful inventions. On May 17, 1918, he was presented with the Willard Gibbs Medal at the meeting of the Chicago Section of the American Chemical Society, and on January 13, 1922, he was awarded the Perkin Medal at the meeting of the American Section of the Society of Chemical Industry held in New York City. These occasions have afforded an opportunity for Dr. Burton to tell of the development and use of his process.

The experimental work started about 1910 when it was clearly seen that the demand for gasoline was to become very large. The cracking of oil-vapors, and the use of various reagents such as aluminum chloride, and ferric oxide was first tried, but the results were regarded as unsatisfactory. Dr. Burton and his associates then decided to attack the problem of pressure-distillation. They realized the hazards of distilling oil at temperatures between 350 and 450° C., where the tensile strength of steel decreases rapidly with rise in temperature, and also where the absorption of carbon was possible with its brittling effect. The deposition of carbon with the consequent overheating of the still bottom offered further opportunity for trouble. Engineers gave them little encouragement, but as Dr. Burton states,[28] "We were able to secure a very liberal sum of money to try the scheme on a large scale, and the worst that could happen would be to burn up our plant and fail in our efforts. So we went ahead."

The first experimental still was made with welded joints and had a capacity of about 100 gallons. The raw material first tried was residuum or crude oil from which the lighter valuable products had been removed. Dr. Burton [28] says, "We soon found that we could not work profitably with this product; when distilled with or without pressure, it produced quantities of coke that deposited on the bottom of ...ill and caused a red-hot bottom that would not stand any rise ... The next proposition comprised the use of high-boiling ...m the crude, viz., oils boiling from 225° C. upwards. We ... distillates at a pressure of about five atmospheres, and

... Tech., 1 (1915), 177.
... Chem., 10 (1918), 484-6.

were thereby able to hold down the temperature to a moderate figure, the cracking being done in the so-called liquid phase. We found to our intense gratification that the low-boiling fractions produced belonged mostly to the paraffin series, which were easily deodorized and finished into products suitable for sale. Further, the yield of salable liquid was good and the production of fixed gases and coke was small. Experimentally, therefore, our work was successful.

"The first large still was 8 ft. in diameter and 20 ft. long, built of ½-in. mild steel plate. The charging capacity was 6,000 gallons or four-fifths of the actual volume of the still. The factor of safety used in design was 5, that is, bursting pressure was taken as 500 pounds per square inch, and the cracking pressure as 100.

"The first difficulty encountered was leakage around the rivets and along the seams. The workmanship on the still was excellent, but oil at high temperatures and pressures was found to leak out far more easily than water. At first, boilermakers looked askance at the job of calking the leaks of a pressure-still, and in many cases when one leak was calked, another formed as a result of the work. The problem was solved when it was found that as the still remained in service the leaks were automatically stopped by carbon deposits.

"Other problems arose. A safety valve that would operate surely in spite of heat and carbonaceous deposits had to be designed. Some oils evolved more gas during cracking than was required to maintain the required 5 atmospheres pressure. Other oils did not evolve enough gas to keep up the pressure. This difficulty was overcome by connecting a number of stills in such a manner that the superfluous gas from some made up the insufficiency of others.

"It was also learned that a dephlegmating system was necessary, when operating at moderate pressures, to separate the light fractions and to return the heavier to the still.

"The first 6,000 barrel still was charged with 'fuel-oil' ranging in boiling point from 200° to 350° C. A 'substantial yield' of a product boiling from 50° to 200° C. was obtained. The loss averaged less than 3 per cent. The high-boiling residue from the still was similar to natural asphalt, and Dr. Burton says, 'Evidently we were doing artificially what Nature had done in ages gone by, viz., distilling petroleum under pressure.'"

A number of runs were made with the 8 x 20 ft. still. These were so successful that Burton requested an appropriation of $1,000,000 to build 60 pressure stills 8 x 20 ft., each of which would be charged with 8,000 gallons of raw material. He says, "Considerable argument was necessary to convince any of our directors that such a revolutionary proposition could possibly be successful, but finally they voted in favor of it, and we went ahead."

Dr. Burton states that the larger difficulties had been overcome at this stage, but that many smaller ones remained. In order to have the best results, the stills must be operated at temperatures between 370° C. and 400° C. At 450° C. steel begins to lose its tensile strength. The

human element enters to a large degree, but according to Dr. Burton eight years elapsed with hundreds of stills in daily use before a fatal accident occurred.

In passing, it may be remarked that this is quite in contrast to reports that circulate about the safety of the Burton process.

Pressure-stills in service at the refinery of the Standard Oil of Indiana increased in number until in 1921 there were 800, with a gross charging capacity of 8,000,000 gallons. Licensees under the Burton patents are operating in equal number.

The daily production of gasoline from Burton stills is 2,000,000 gallons out of about 12,500,000 gallons daily output of the United States and Canada.

U. S. Patents have been issued to Burton,[29] Humphreys,[30] Clark,[31] and Hopkins,[32] covering the basic idea and the various improvements and developments of the process and apparatus.

The original Burton patent, No. 1,049,667, states that the object of the invention is to provide a method of converting fuel- and gas-oils into low boiling products of the "same paraffin series."

"This object I accomplish by raising the boiling point of the liquid residue and increasing the heat-influence thereon while undergoing distillation by maintaining back-pressure on said liquid of the vapors rising therefrom by distillation, as has hitherto been done as aforesaid, and also maintaining the vapors themselves under pressure throughout their course from the still through the condenser and while undergoing condensation."

The claims of the patent are two in number, and read as follows:

"1. The method of treating the liquid-portions of the paraffin-series of petroleum-distillation having a boiling point upwards of 500° F. to obtain therefrom low-boiling-point products of the same series, which consists in distilling at a temperature of from about 650° to about 850° F. the volatil constituents of said liquid, conducting off and condensing said constituents, and maintaining a pressure of from about 4 to about 5 atmospheres on said liquid of said vapors throughout their course to and while undergoing condensation.

"2. The method of treating the liquid-portions of the paraffin-series of petroleum-distillation having a boiling point of upward of

[29] (Burton), U. S. Patents: 1,049,667, Jan. 7, 1913, "Manufacture of Gasoline." 1,055,707, Mar. 11, 1913, "Process of Producing Asphalt." 1,105,961, Aug. 4, 1914, "Manufacture of Gasoline." 1,112,113, Sept. 29, 1914, "Process for Producing Gas from Hydrocarbons." 1,160,689, Nov. 16, 1915, "Method of Safeguarding Stills." 1,167,884, Jan. 11, 1916, "Petroleum Product."

[30] (Humphrey), U. S. Patents: 1,119,700, Dec. 1, 1914, "Method of Distilling Hydrocarbons." 1,122,002, Dec. 22, 1914, "Petroleum Distilling Apparatus." 1,122,003, Dec. 22, 1914, "Process of Distilling Petroleum." 1,343,674, June 15, 1920, "Distillation of Petroleum Oils."

[31] (Clark), U. S. Patents: 1,119,496, Dec. 1, 1914, "Method of Distilling Petroleum." 1,129,034, Feb. 16, 1915, "Art of Petroleum Distillation." 1,132,163, Mar. 16, 1915, "Art of Petroleum Distillation." 1,388,514, Aug. 23, 1921, "Distillation of Petroleum Hydrocarbons."

[32] (Hopkins), U. S. Patents: 1,119,463, Sept. 26, 1916, "Process of Distilling Petroleum." 1,119,464, Sept. 26, 1916, "Apparatus for Distilling Petroleum."

500° F. to obtain therefrom low-boiling-point products of the same series, which consists in distilling off at a temperature of from about 650 to about 850° F. the volatil constituents of said liquid, conducting off and condensing said constituents, maintaining a pressure of from about 4 to about 5 atmospheres on said liquid of said vapors throughout their course to and while undergoing condensation, and releasing from time to time accumulations of gas from the products of condensation."

The first Burton stills, built in 1913, were of about 250 barrel gross capacity. The shell and ends were made of ½- to ⅞-in. mild steel plate, riveted, and carefully calked, or better still, "hammer welded." [33]

The stills were provided with a safety-valve, draw-off line for hot residuum, inclined vapor line that functioned also as a dephlegmator, condenser, a small tank to act as a gas-liquid trap and separator, and relief valves for gas and liquid.

The still was charged and heated to 650 to 675° F. whereupon cracking commenced. The pressure was built up to 75 to 80 lbs. per sq. in. by the gases evolved. Distillation proceeded slowly over a period of 48 hours in which time the temperature rose to about 800° F., and 60 per cent of light distillate was collected. The heavy residue in the still held a granular carbon, or at least highly carbonaceous substances, in suspension. The residue was charged into stills where it was run to coke. The coke so formed was equivalent to 5 per cent of the oil charged into the coking still. The distillate from the coking still was found to be peculiar in that for a given specific gravity its viscosity was very low. This distillate, as a product, is the basis of Burton's patent 1,167,884. It may be run again in the cracking stills, or used for other special purposes.

One of the main sources of difficulty lay in the deposition of the granular carbon on the still bottom. Circulation of the liquid is poor in any simple still, and if the application of heat for any reason becomes less vigorous, and the movement of the oil for this or any other reason is slow, the carbon will settle on the bottom of the still. Once it has settled, there is no feasible way of getting it in suspension again. The deposit of carbon is an effective heat insulator, and as a result the bottom plate of the still soon develops a hot spot. In a still operated at ordinary pressure this is not serious, although it causes deterioration of the plate by oxidation. But with pressure in the still hot-spots are not allowable. The fire must be drawn, the still cooled, and the carbon deposit removed.

[33] Much is claimed for the "hammer-welding" process that consists in lapping the square edged plates, carefully heating them in a reducing gas flame and then vigorously working the weld with heavy high-speed power hammers to properly shape the joint and to refine the grain. The exponents of this method of welding are possibly overly enthusiastic about the superiority of their methods over other methods of welding. I am familiar with extensive tests of welding methods that showed conclusively that acetylene welds were 80 to 100 per cent strong, depending on how the weld was built up, and absolutely reliable. Electric welds were found to be only 60 per cent strong, but were also reliable. Forge welds were only 50 per cent strong and were most unreliable. There is no doubt but that mechanical working through the critical range is beneficial in all instances.

In order to avoid this difficulty hinged false-bottom plates were introduced into the still. This improvement is covered in Patent 1,122,002 granted to Mr. Humphreys, who states that previously they had been able to distill only about 1/3 of the oil from the still before it was necessary to shut down owing to the deposition of carbon, but that by using the false-bottom plates 2/3 of the oil could be distilled. This increased the time of distillation from the 24 hours required to distill 1/3 of the oil to about 48 hours.

The patent of Humphreys 1,119,700 provides for the use of an inclined pipe "run-back" which should function as a partial condenser returning the heavier hydrocarbons of the vapor to the still.

The use of catalytic metal plates is the basis of Humphrey's Patent No. 1,122,003. He states, "The catalytic surfaces may be of metal, such as steel, brass, or copper, either in the form of plates or gauze, although mineral fibers such as asbestos or glass wool seem to be equally effective. The action of those surfaces, like that of most catalyzers, is obscure, but it is a fact that when the catalyzing surfaces are used, the action is so augmented that 65 to 70 per cent of the contents of the still can be satisfactorily transformed in the desired manner before it becomes necessary to draw off the residue, while without them, only about one-third of the charge can be so transformed. It seems to be immaterial whether the hydrocarbon is in liquid or vapor form when brought in contact with the surfaces." The false-bottom plates may be the catalytic plates, or these latter may be hung from the upper part of the still.

When a pressure-still is charged and brought up to the boiling point of the raw material, it is necessary to conduct the further heating under pressure in order to prevent the distillation of heavy oils from the still. Clark's Patents Nos. 1,129,034 and 1,132,163 cover the manifolding of the condensers in such a manner as to allow establishment of working pressure on a freshly charged still by means of the gas evolved by stills that are partly run-down.

A. S. Hopkins in Patents 1,199,463 and 1,199,464 calls attention to the heat losses, and also the difficulty of accurate control attendant upon the use of air-cooled run-back pipes and dephlegmators. In these patents, he claims the use of a process and apparatus that consumes this heat and allows of accurate regulation. His dephlegmator is cooled by the raw material that is fed to the still.

U. S. Patent No. 1,160,689 covers a method of venting the gases from pressure-stills when the pressure becomes excessive. Provision is made for expansion and cooling in such a manner as to avoid ignition of the hot combustible gas.

The principal features of the simpler type of pressure-still apparatus is shown diagrammatically in Figure 112, taken from the Humphreys-Burton Patent 1,343,674. This patent covers, in particular, the apparatus for automatically controlling the firing of the still. The oil is charged into the still which is heated by a fire on the grate of the automatic stoker. The still is fitted with a safety valve, and with an

inclined vapor-line leading to the air cooled partial condenser. About three-fourths of the vapor condenses here and runs back to the still to be treated further. The balance of the vapor passes the pressure-control valve to the water-cooled condenser. The liquid and gas from this condenser enter the receiving and separating drum, from which the condensate is trapped off. The gas flows through an absorption tower in which it is scrubbed by downwardly flowing naphtha or oil. In this manner the hydrocarbon vapors are removed from the non-condensible gases.

The use of a pressure-relief valve between the air-dephlegmator and the water-condenser is not in conformity with the basic Burton Patent 1,049,667 in which the position of this valve beyond the water-condenser is stressed as being of the essence of the process. Is this perhaps a recognition of the fact often stated by refinery engineers that condensation under pressure has no effect other than that of causing the most volatil hydrocarbons to condense?

For six or seven years the Standard Oil Companies have used a still not unlike a Heine boiler. This apparatus is covered by U. S. Patent No. 1,388,514 granted to E. M. Clark and shown in Figure 113. The oil is heated as it circulates through the tubes. The body of the still is not exposed to the hot gases. The claim is made that oil equivalent in volume to twice the charging capacity of the still can be added during the normal operating period of the still. The total distillation period is not much longer than that of the ordinary Burton still. Thus, the capacity of the still is almost trebled, to say nothing of the greater safety of operation resulting from the fact that no hot-spots can form on the still-bottom. The additional oil is run in at the top of the inclined vapor-line, and is supplied in an amount roughly equal to the volume of light distillate formed concurrently.

The advantages of the tubular-still appear to be:

1. The more effective absorption of heat from the hot furnace gases, as a result, in part, of the larger heating surface, but more particularly because of the more rapid circulation of the heavy oil, and of the less deposition of carbon in the heating surface.

2. Greater safety and facility of operation because hot-spots on the still-bottom are not possible.

3. Deposition of carbon as the oil with carbon in suspension moves slowly through the still. The carbon deposited in the still does little harm.

4. Larger output in a given time.

A further improvement of the Clark apparatus lies in the use therewith of the Hopkins' dephlegmator, or of a dephlegmator or evaporator into which crude oil may be fed as is now done at the plant of the Standard Oil of Kentucky, built a few years ago at Louisville.[34] This plant is shown in Figure 114. The scheme of running crude oil to the pressure-stills in use at this plant was devised by A. K. Whitelaw. The heat in the vapors from the still is used to evaporate distillate equiva-

[34] *Nat. Pet. News,* Mar. 4, 1921, 52-5.

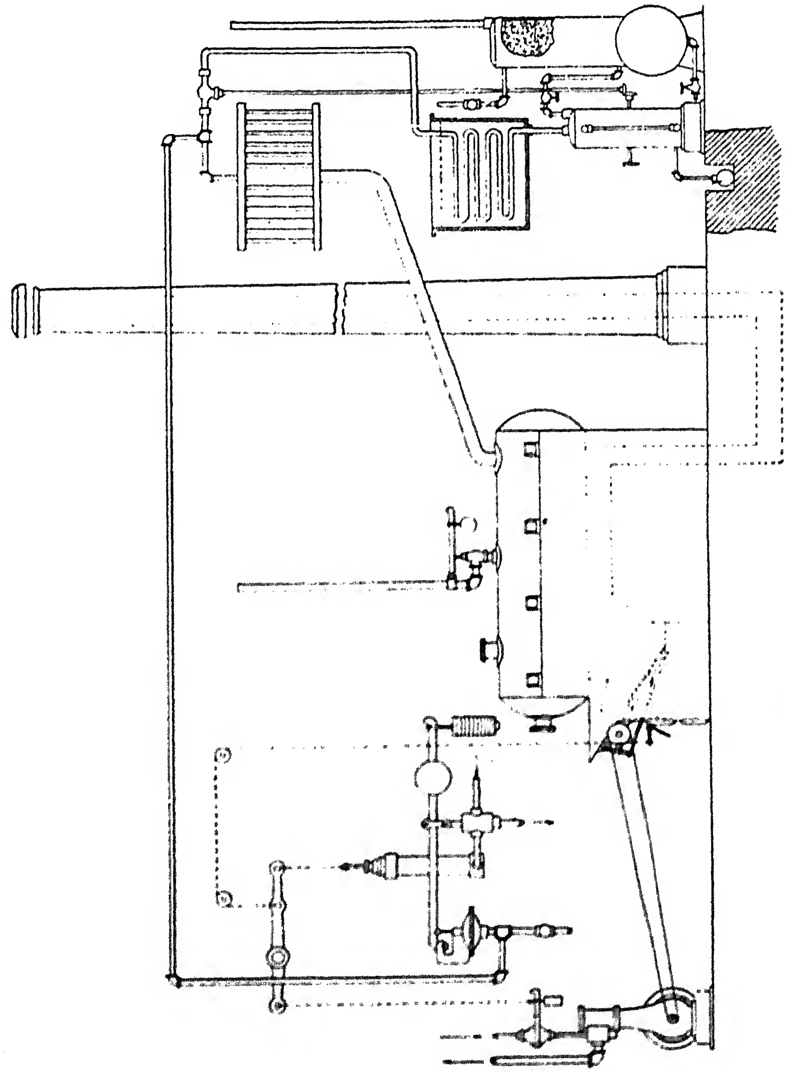


Fig. 112.—Burton Cracking Still and Accessory Equipment.

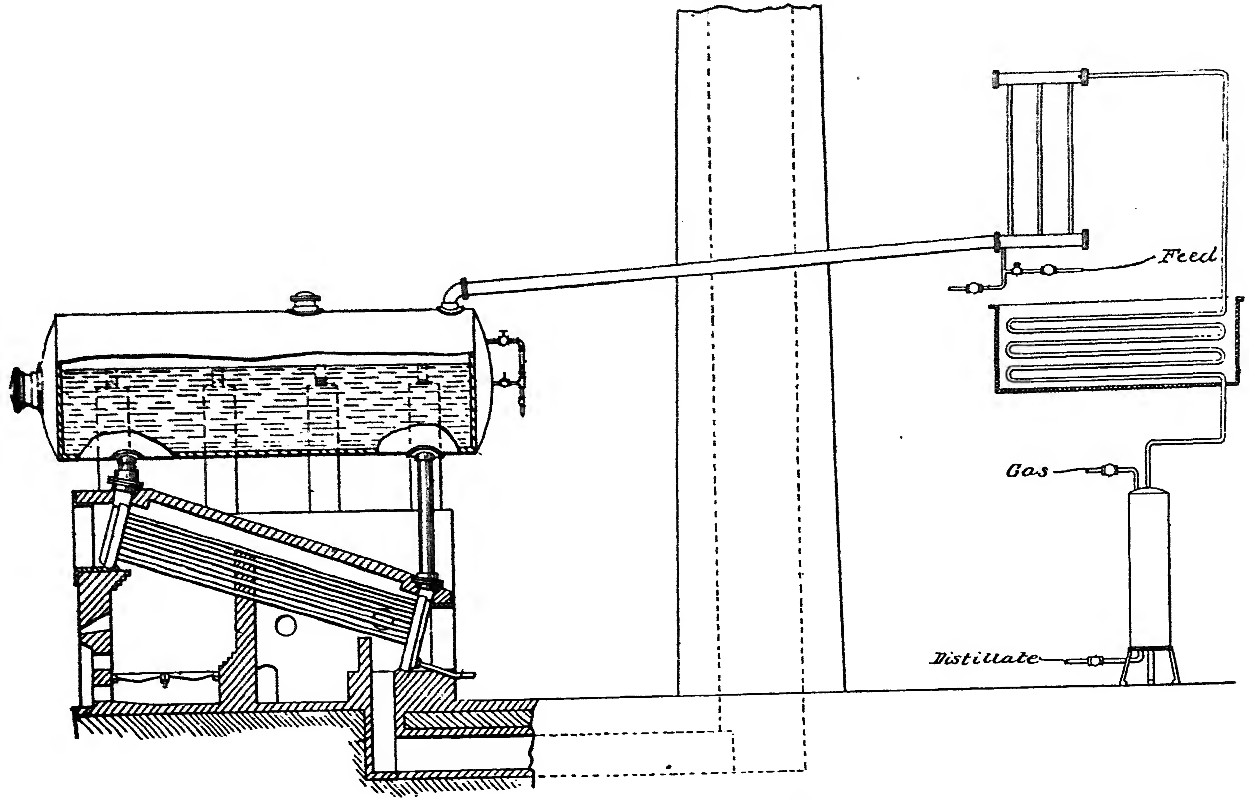


Fig. 113.—Burton-Clark Tubular Still.

lent to about one-quarter of the volume of the crude oil. The plant is said to handle 5,000 barrels of crude oil per day in 60 pressure-stills.

Summary of Operating Conditions and Yields—Burton Process.

The ordinary Burton still is of about 250 barrel gross capacity, charged with 200 barrels of gas-oil or similar distillate, heated slowly to 250° F. at atmospheric pressure to remove water, placed under 75 to 80 lbs. pressure, heated to an initial cracking temperature of 675° F., and slowly distilled at rising temperature for a period of 40 to 50 hours unless the run is prematurely terminated by deposition of carbon and development of a hot-spot on the bottom of the still. The temperature is raised 100 to 125° F. during the distillation, and a pressure-still distillate equivalent to 60 to 65 per cent of the volume of the oil charged is raw material. Upon subsequent distillation 50 to 55 per cent of the pressure-still distillate is obtained as a gasoline of 440° F. end-point. The yield of gasoline in a single pressure-distillation is thus 30 to 35 per cent. The "unsaturation" of this gasoline as determined by the use of concentrated sulfuric acid is 10 to 12 per cent. At the conclusion of each run, the still must be cooled and cleaned.

The use of the tubular still, operated semi-continuously, results in more than doubling the output of a still in a given period of time. Automatic and accurate control of pressure are essential to obtaining the largest yields of the best quality of product.

The distillate is condensed under pressure if the process is conducted as specified in all patents except one. In this instance the gases are scrubbed to remove the light gasoline.

The following analysis is typical of the fixed gases formed:

	Per Cent
CH_4	56.4
C_2H_4	25.8
C_2H_6, etc.	8.5
CO	0.8
H_2	7.4
Other	1.2
Total	100.0

A battery of ordinary Burton stills in the refinery of the Standard Oil Company of Ohio plant at Casper, Wyoming, is shown in Figure 115.

The Holmes-Manley and Other Cracking Processes Controlled by the Texas Co.

The recent agreement[84] between the Texas Company and the Standard Oil Company of Indiana has already been mentioned. In addition to the Hall process and the Gray $AlCl_3$ process, the Texas

[84] *N. Y. J. Com., Nov. 8, 1921.*

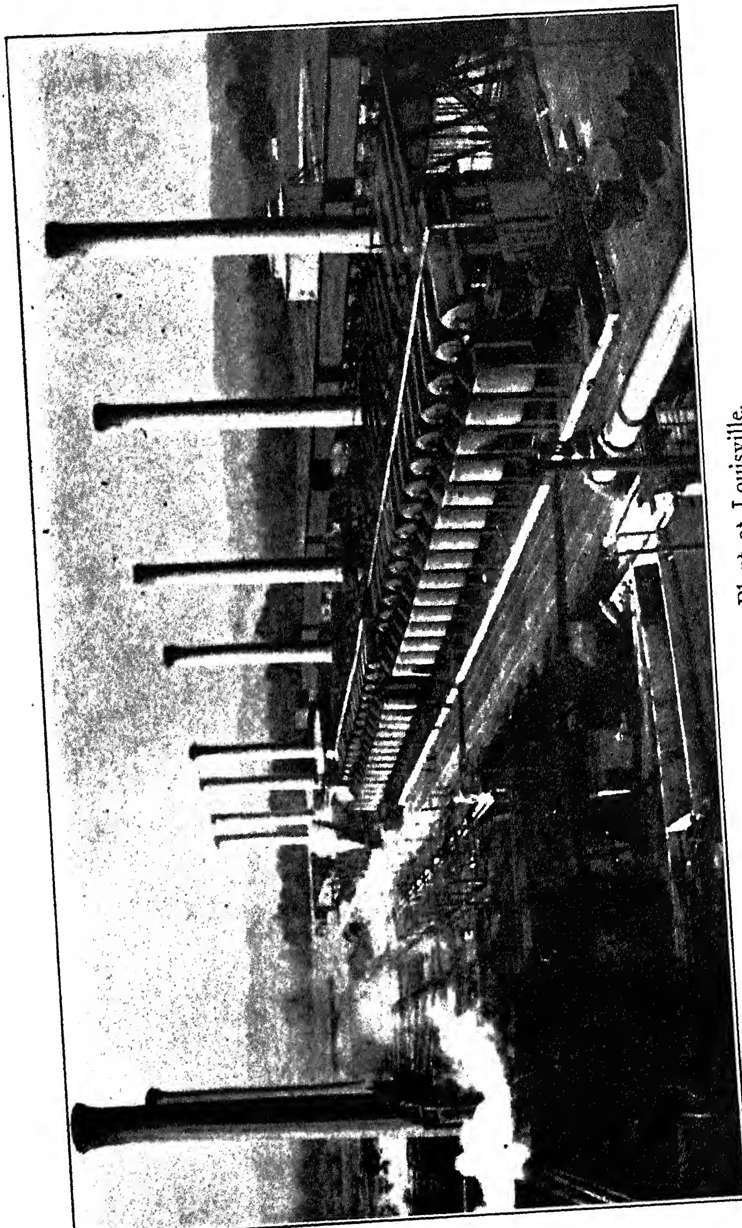


Fig. 114.—Burton Plant at Louisville.

Company controls the J. H. Adams and the Holmes-Manley pressure-still processes. The agreement provided that each company shall have the right to operate under the patents of the other covering the cracking of oil under pressure. Each company, upon an agreed division of royalties, may also license others to operate under any or all of the patents.

Twenty-four batteries of the Holmes-Manley vertical cracking stills were completed in December, 1920, at the Port Arthur refinery of the Texas Company.[36] These are shown in Figure 116. A battery consists of four stills, each 3 ft. in diameter, 40 ft. long, set vertically, and provided with a scraper arrangement for removing carbon from the sides. The operating pressure is about 175 lbs.

The first battery was put into operation in February, 1920. During the year 1920, 2,295,147 barrels of gas-oil and similar distillates

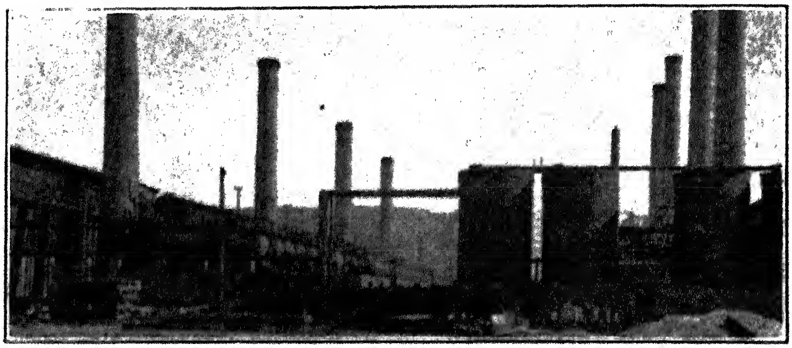


FIG. 115.—Burton Stills at Casper.

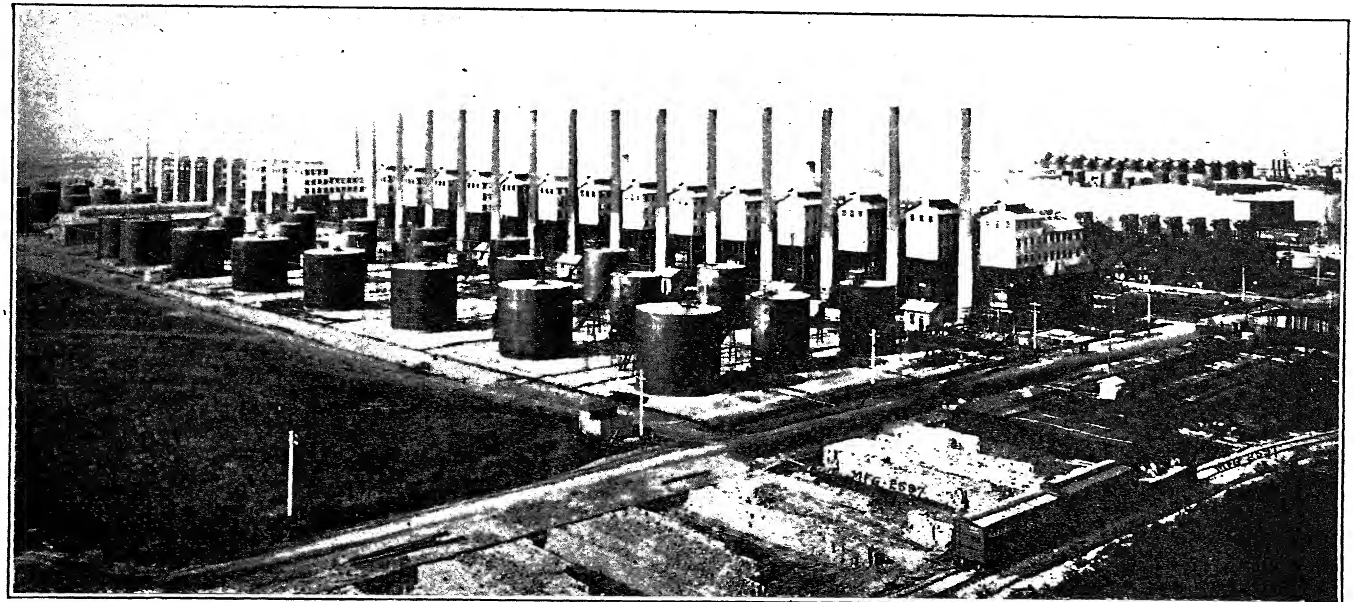
were charged to these stills, and in 1921, 5,050,798 barrels. Much of this oil was what is known as "cycle" stock, that is, distillate produced
'oms to coke. Twenty-seven per cent of
•ted into gasoline passing the New Navy
is said to be highly profitable.
.I. Adams, covering ground very similar
lso controlled by the Texas Company.
' ratents antedated Burton's application.

The Fleming Process.

The Fleming process is the invention of Mr. Richard Fleming, and is now controlled by The Richard Fleming Company of 140 Cedar Street, New York City, and sponsored by the M. W. Kellogg Company

[36] *The Texaco Star*, 9 (1922), 12-15.

[37] U. S. Patents: 976,975, Nov. 29, 1910, "Oil-Converting Process." 1,320,-354, Oct. 28, 1919, "Oil-Converting Apparatus." 1,320,354, Nov. 4, 1919, "Process for the Conversion of Liquids, Fuels, and Oils." 1,320,727, Nov. 4, 1919, "Apparatus for the Conversion of Liquids, Fluids, and Oils." 1,327,263, Jan. 6, 1920, "Process for the Conversion of Liquids, Fuels, and Oils."



Courtesy of the Texas Company.

FIG. 116.—Holmes-Manley Plant of the Texas Company.

of New York City. Three U. S. Patents[38] have been issued covering the process and apparatus. The estimated cost of a 10-still plant is $350,000. This plant would have a daily capacity of about 1500 barrels of raw material.

One Fleming unit has been operated at the plant of the Shell Company of California at Martinez, six at the plant of the Sterling Oil and Refining Co., of Wichita, Kansas, and 18 at the plant of the Marland Refining Company. Two units are being built for the Grayburg Oil Company, two for the Star Refining and Producing Company, and one for the Portland Oil and Refining Company.

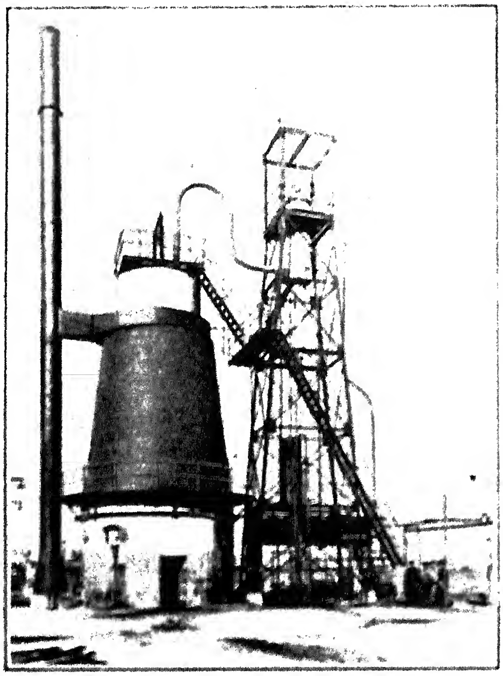


FIG. 117.—Fleming Cracking Unit.

The following description of the process is partly taken from notes kindly furnished to me by the M. W. Kellogg Company. I am also indebted to them for the photograph of a Fleming unit reproduced as Figure 117. The process and apparatus are also described by V. B. Guthrie.[39]

The still proper is a hammer welded steel drum 10 ft. x 30 ft. set on end in a furnace. Thirty-inch manholes are provided on the top and bottom. In accordance with the experience gained in the manufacture of pressure stills for various processes, the shell is 1 in. and the head 1½ in. in thickness. Thus the effect of temperature on the metal and the corrosion due to vapors are taken into consideration. The bottom head of the still is not heated. The lower part of the side-walls is protected by a layer of firebrick. The still should have a life of ten years in the original position and may then be up-ended for further active service. Four fuel-oil burners, so set as to give a tangential and rotary movement to the products of combustion, are now used, but the furnace can easily be modified by installing Dutch ovens to use coal in those localities where this is more economical. The furnace is so

[38] U. S. Patents: 1,324,766, Dec. 9, 1919, "Process of Conversion of Hydrocarbons." 1,325,668, Dec. 23, 1919, "Process of Condensing and Treating Distillates." 1,394,987, Oct. 25, 1921, "Apparatus for Condensing and Treating Distillates."

[39] *Nat. Pet. News*, June 28, 1922, 23-27.

designed that the entire circumference of the still, except for a very few feet at the bottom and top, is swept by the flue-gases. The efficiency may be judged from the fact that the flue-gases leave the setting only 100 to 150° F. hotter than the contained oil.

From the still the vapors pass to the bottom of the dephlegmator through a vapor-line that is bent into a goose-neck in order to allow expansion. The dephlegmator is 3 feet in diameter, 12 feet long, made of ½-in. plate, and fitted with perforated circular baffle-plates.

Gas-oil on its way to the still, in an amount of about 6 gallons per minute, is pumped into the top of the dephlegmator. To furnish additional cooling an auxiliary stream of cooled oil is circulated through the dephlegmator and thence to a water-cooled coil. The flow of this oil is controlled separately from that going to the still. The vapor from the still enters the dephlegmator at about 700° F., and as a result of its contact with the downwardly trickling gas-oil is cooled and leaves at about 400° F. Four-fifths of the vapor is condensed and runs back to the still.

The vapors leaving the dephlegmator are condensed in an apparatus of the jet type. The arrangement is such that a needle-type valve releases the vapor between two cones of water. It should be noted that the still-pressure is maintained up to the needle valve, but that in the throat of the condenser itself there is no pressure—in fact, readings taken show a slight vacuum. The pressure on the oil in the still is 100 pounds per square inch.

The combined water and condensate, looking almost like milk, are led through a tank where the water, condensate, and fixed gases separate and are drawn off. About 2000 cu. ft. of 1100 B.t.u. gas are produced each hour by a single cracking-unit. Losses compare favorably with those in other processes. There is no appreciable absorption of gas by the condenser water. The solvent effect of the water is claimed to be valuable, aiding materially in cleaning up the distillate and reducing later treatment.

The still is operated on the batch principle, with an original charge followed by make-up oil as the vapors are distilled. Typical log sheets taken at the Martinez plant show the following:

Charge 295 Barrels, and 300-350 Barrels of make-up oil per run. The time required for the complete cycle is as follows:

	Hours	Minutes
Charging	1	10
Raising to pressure	11	..
Actual running	48	..
Cooling and relieving pressure	3	..
Removing residue	1	..
Steaming, closed covers	..	30
Opening still	..	45
Steaming, open covers	..	15
Cooling	7	..
Cleaning	4	..
Closing covers	1	..
Total time from charge to charge	77	40

During the three hours required to relieve the pressure, a second distillate is obtained that is almost identical with the original gas-oil, and is used in succeeding runs. The cooling period has been greatly shortened by the use of a rotary sprinkler or spray of water inside the still.

The coke forms loosely on the bottom and sides of the still, and is removed from the bottom manhead. The amount varies between rather wide limits, 36 lbs. and 550 lbs. both having been observed. An average figure is 350 lbs. when California distillates are cracked. It is rarely baked on the shell in such condition as to require a chisel and sledge for its removal. Scraping from a platform raised and lowered from the top manhole usually suffices. From the above data, it is evident that each unit can be used for 95 to 100 runs per year.

The gas-oil used at Martinez was a product from California crude.

	Degrees
Gravity	26.5-27.5 Bé.
Initial B. P.	392° F.
80% over at 353° C.	672° F.

Typical results obtained from cracking 27° Bé. California distillate are:

	Per Cent
Light cracked-distillate	54.5
Distillate to be re-cracked	19.4
Heavy fuel oil	21.3
Loss	4.8

The light cracked distillate has the following properties:

	Degree
Gravity	40-44 Bé.
Initial B. P.	140° F.
Final B. P.	582° F.

…t into gasoline and distillate to be re-cracked. The net result …rations may be summarized as follows:

	Per Cent
	35.3
…o be re-cracked	36.0
	21.3
	7.4
	258 lbs.

The gasoline referred to has a gravity of 48 to 50° Bé., an initial boiling point of 140° F., and an end point of 428° F. It should be noted that California gasolines run 8 to 10° Bé. heavier than Mid-Continent gasoline of the same distillation range.

The consumption of fuel oil at the Martinez plant is equivalent to 4 per cent of the oil charged to the still. At the Wichita plant of the Sterling Oil and Refining Company it runs 7 to 9 per cent.

The tabulation that follows is a summary of the operations of a run at the Wichita plant using Mid-Continent gas oil as raw material:

Pressure used—pounds	110
Initial charge—bbls.	317
Fed during run—bbls.	243
Total charge—bbls.	560
Gravity of oil charged initially	33.7° Bé.
" " " fed during run	33.7° Bé.
Light cracked distillate produced—bbls.	270
Gravity of light cracked distillate	56.6° Bé.
Per cent of light cracked distillate distilling below 419° F.	75.0
Heavy-distillate—bbls.	60
Gravity of heavy distillate	36.0
Still-bottoms—bbls.	194
Gravity of still bottoms	20.7° Bé.
Pounds of coke	1150
Loss—bbls.	27
Loss, as per cent of total charge	4.8
Fuel used—bbls.	50
Fuel used—per cent of total charge	8.9
Time, running	39 hrs. 15 min.
Time, cleaning	3 hrs. 50 min.
Time, total cycle	70 hrs. 30 min.
Gasoline produced—bbls.	200.5
Gasoline produced—per cent of total charge	35.8
Kerosene produced—per cent of total charge	12.5

The reader will note that the weight of the coke produced in cracking the Mid-Continent distillate is roughly three times that produced from California distillate. An average coke formation in Mid-Continent practice is 1000 lbs. per run.

The Cross Process.

The Cross process[39a] is the invention of Drs. Walter M. and Roy Cross. It is covered by several U. S. Patents,[40] and also by several applications pending in this and foreign countries. The patents have been assigned to the Gasoline Products Company of New York City.

The inventors of this process believe that the theoretically correct method of converting heavy hydrocarbons into gasoline is to apply

[39a] I am indebted to Dr. Roy Cross for information relative to the Cross process. Descriptive articles have appeared in the *Nat. Pet. News* for May 3, 1922, and April 26, 1922.

[40] U. S. Patents: 1,203,312, Oct. 31, 1916, "Process of Treating Hydrocarbons and Products Derived Therefrom"—Walter M. Cross. 1,255,138, Feb. 5, 1918, "Method in the Treatment and Refining of Petroleum."—Roy Cross. 1,326,851, Dec. 30, 1919, "Process of Treating Hydrocarbons."—Walter M. Cross.

heat to the liquid. This of course is done in the Burton and other pressure-still processes operating at pressures of 75 to 100 lbs. per sq. in. These pressures are sufficient to prevent the too rapid vaporization of the heavier hydrocarbons, but the gasoline, kerosene, and even the lighter part of the gas-oil are vaporized, with consequent absorption of heat from the reaction zone. This necessitates the constant supplying of much more heat than is necessary to bring about the thermal decomposition of the heavy hydrocarbons. In the Cross process a pressure of 600 lbs. or more is used. This is sufficient to keep most of the hydrocarbon material in liquid form and to avoid the absorption of heat that would accompany vaporization. After the reaction period of about fifteen minutes the reaction mixture of light and heavy hydrocarbons and gas is discharged into a cooling coil with release of pressure to about 40 lbs. A "synthetic-crude-oil" is thus obtained that can be handled by ordinary methods. Patents were obtained covering this central idea, and are claimed to be more nearly basic than any other patents covering pressure-distillation processes.

The use of the very high pressure presented difficulties of a practical nature in the design of commercial apparatus. The decision was made to attempt to separate the heating and reaction zones, as is done in some measure in the Clark-still used by the Standard Oil Company. In the Cross process the heating is done in a pipe-still similar in principle to those used in topping plants except that it is carefully designed to stand the high pressure. The hot oil is then discharged into a reaction chamber where the reactions have time to take place. The method has several obvious advantages. The rate of heat transfer will be high as a result of the large heating surface, and the relatively high velocity of oil in the pipe-coil. It is claimed that little carbon collects on the walls of the heating coil. This is partly because of the short time of contact, partly because the oil is heated to reaction temperature in only the last few lengths of this coil, and more particularly because the velocity of the oil keeps the carbon in suspension in the oil.

The apparatus used in the Cross process is shown diagrammatically in Figure 118. A layout of a double unit is shown in Figure 119.

A hydraulic pump, equipped with a regulator, forces the gas-oil or other distillate through the heating coil. The part of this coil above the upper arch of the furnace is called the preheater, and consists of twenty-eight 20-ft. length of pipe of approximately 4-in. internal diameter and ½-in. wall thickness. Cast iron plates fit over the ends of each pipe in such a manner that when the pipes are arranged in a heating bank the ends are protected from the hot furnace-gases. Special return bends are used to connect the pipes into a continuous coil.

From the preheater the oil passes to the lowest row of pipes in the heater-coil. This is another continuous coil constructed in the same manner as the preheater. The life of the heater tubes is said to be about 18 months. A tube can be replaced in one day.

The oil enters the preheater at ordinary temperatures, leaves the preheater at about 400° F., and leaves the heater coil at about 875 to 925° F.

The temperature of the oil leaving the heater coil is used as a criterion for control. If the temperature is too high the rate of flow is increased and vice versa. The temperature in the furnace itself is held at almost 1,350° F.

The heating furnace is enclosed by walls made of one course of common brick and lined with a single course of fire brick. The ends of the heating coils are easily accessible through hinged sheet iron doors. The furnace is so designed that it can be quickly cooled in order to allow quick cleaning or tube replacements.

The hot oil leaving the heater coil enters the reaction chamber. This was formerly a 30-in. diameter steel chamber 40 ft. long. The walls were [illegible] in. thick, and all seams were hammer welded. A seam opened on one occasion, and, although no serious damage was done, several

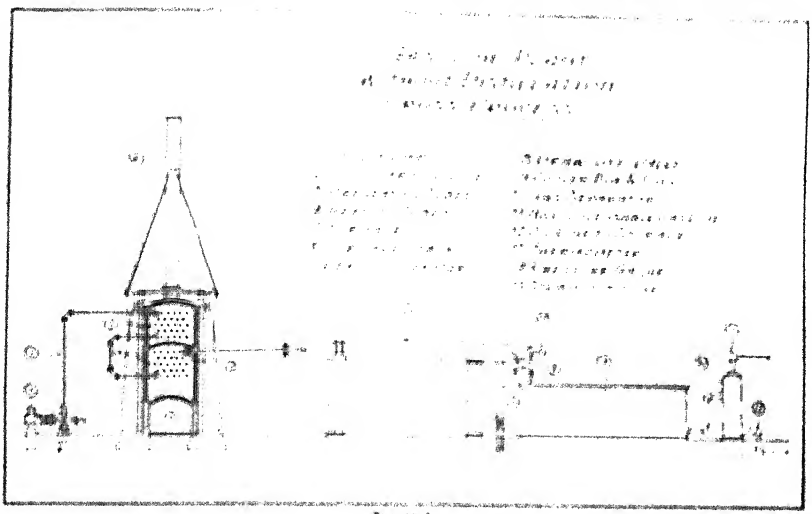


Fig. 118. Diagram of Cross Process Plant.

days were required to make the necessary repair. The reaction chambers now used are 40 in. in internal diameter and 40 ft. long. The walls are 3 in. thick. They are forged by the Midvale Steel and Ordnance Company from a single ingot, in much the same manner as large naval guns. No heat is applied to the reaction chamber, but it is heavily lagged to prevent excessive heat loss.

The entire time required for the oil to pass through the preheater and heater coils is only 1¼ minutes. However, the oil is above reaction temperature (675° F.) only about 20 to 25 seconds. This explains the small amount of decomposition that takes place in the heating coils. The reaction chamber is made large enough so that a period of 15 to 60 minutes (depending on how much carbon has deposited in the chamber) is allowed for the chemical change at a temperature of 875 to 925° F. The vapor above the oil is composed mainly of permanent gases. Gas

and liquid leave the chamber through a 1-inch line connected so that the reaction chamber is kept one half full of liquid. The level is automatically maintained, for should the liquid level rise no gas would escape, and the gas pressure would build up. But the relief valve is set at about 600 lbs., and hence the pressure of the gas would blow the liquid out until the liquid level returned to a point such that both gas and liquid could escape. The small volume of oil in the entire apparatus at any instant is emphasized as an important advantage from the standpoint of possible fire damage.

The escaping liquid and gas after passing the pressure release valve enter an immersed cooling coil. Forty pounds pressure is maintained until gas and liquid have been passed through a separator. The gas is used for fuel and supplies about half of that required for heating the furnace. Recently the oil and gas from the reaction chamber have been run directly to a still so that the heat contained in them could be utilized to vaporize the lighter fractions.

The plant at the Lawrenceville, Illinois, Refinery of the Indian Refining Company was customarily run three or four days and then necessarily shut down one day for cooling and cleaning the carbon from the reaction chamber. The newer plants with the large forged reaction chamber will be operated continuously for six days and cleaned on the seventh.

A single passage of gas-oil through the apparatus results in the formation of about 30 per cent of standard gasoline. If kerosene is used as a raw material the gasoline yield is 40 to 45 per cent.

If gas-oil is cracked once, the synthetic crude distilled, the heavy portion re-cracked, and so on, the ultimate yield of gasoline is about 65 per cent. At the same time there will be produced in all 25 per cent of fuel-oil, and 10 per cent by volume of the original oil will be "lost" in the form of carbon and gas.

If heavy fuel-oils and residuums are to be handled it is necessary to run them to coke in a coking-still, and then crack the distillate. If the heavy fuel-oils or residuums are cracked directly the tubes and reaction-chambers are rapidly clogged with carbon.

Data covering a single cycle cracking operation are given below.

Run No. 44. Jan. 21, 22, 23, 24, 25, 1922

Oil used as raw material	3,039 Bbls.
Synthetic crude produced	2,909 "
Loss	4%
Gasoline produced (727 barrels)	24%
Fuel used	91 Bbls.
Fuel used per barrel of gasoline made	0.125 Bbls.
Hours on stream	96
Hours on fire	98
Oil cracked per hour	31.5 "
Maximum oil temperature	915° F.
Average oil temperature	900° F.
Maximum furnace temperature	1,375° F.
Maximum stack temperature	765° F.
Average stack temperature	740° F.
Pressure	600 lb./sq. in.

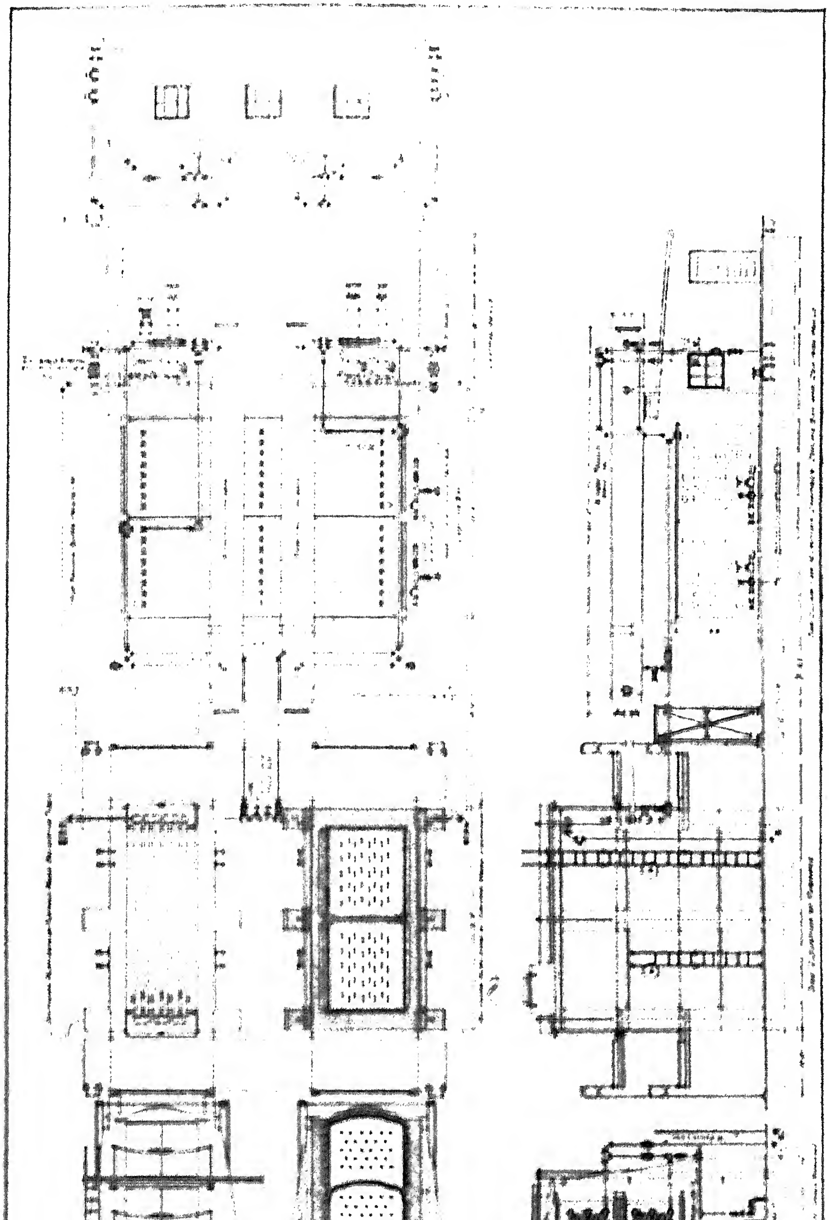


FIG. 119.—Double Unit Layout of Cross Process.

The following cost data are given by Dr. Cross:

DETAILED COST OF MAKING ONE BARREL OF GASOLINE BY CRACKING

	Cross System	Pressure Distillate System
Labor	$0.24	$0.70
Materials	0.06	0.06
Fuel oil	0.20	0.40
Overhead	0.16	0.16
Fixed charges (25% of cost of plant per year)	0.20	0.60
Rerunning	1.20	1.20
Gas-oil equivalent to converted gasoline	1.25	1.25
Refining loss (1-6 barrel)	0.20	0.20
Degrading of gas oil to fuel oil (¼ barrel)	0.06	0.06
License charges	0.16	0.16
Total cost per barrel	3.73	4.79

The above summary is based upon the operation of commercial plants in the fall of 1921. Gas oil is figured at $1.25 per barrel and fuel oil at $1.00 per barrel.

The following explains the above differences in labor, fuel, and fixed charges:

	Cross System	Pressure Distillate System
Amount of oil treated per unit per average operating day including cleaning.	500 bbls.	150 bbls.
Amount of gasoline produced per day per unit	125 "	50 "
Installation cost of one unit	$40,000.00	$50,000.00
Installation cost per bbl. of oil treated per day	80.00	333.00
Installation cost per bbl. of gas per day	320.00	1,000.00
* Fuel oil required per bbl. of gas produced	0.20 bbl.	0.40 bbl.

* By use of the non-condensable gas the amount of fuel oil required is reduced to 0.16 bbl. of gasoline.

ost of a single Cross unit that will handle 750 barrels of oil pproximately $47,500.00.

commercial unit was built at the plant of the Indian Refin- y at Lawrenceville, Illinois. The Pure Oil Company is building four units at Heath, Ohio, and the Roxana Petroleum Corporation two units at Wood River, Illinois, the Petroleum Refining Company at Latonia, Ky., Globe Oil and Refining Company of Blackwell, Okla., and the Southern Oil Corporation of Yale, Okla., one unit each, and the Sapulpa Refining Company one or more units at Sapulpa, Oklahoma. The process has been licensed to the Royal Dutch Shell, and will doubtless be used by them in many parts of the world.

The Dubbs Process.

The Universal Oil Products Company claims that the Burton process is an infringement on a patent[41] issued to Jesse A. Dubbs, and suit is pending in the U. S. District Court at Kansas City. A plant was built near Santa Barbara, California, in 1909, and an emulsified oil was dehydrated by the process of heating under pressure as described in the patent. The following quotations are excerpts from the specifications and claims of Dubbs' patent.

"This invention relates to improvements in treating oil and refers more particularly to a process of subjecting the oil to heat and pressure.

"Among the salient objects of the invention are to provide an improved method of treating oil wherein both the vaporization and condensation take place under the pressure of the generated vapors; to provide a method which is particularly adapted for the removal of the finely divided particles of water from emulsified hydrocarbon oils; to provide a method which will permit of the oil being continuously subjected to the required heat and pressure in both the still and condenser without the interruption of its flow; to provide a method by which this may be safely and economically done and in general to provide an improved method of the character referred to."

In all there are eleven claims. The apparent object of the process was to provide a feasible means for dehydrating heavy emulsified oil.

The results of experiments in which the process was applied in the cracking of a 16.6° Bé. Mexican fuel oil, and a 25° Bé. mixture of Healdton, Peabody, and Cushing crude are described by Gustav Egloff.[42] The oils were passed through a heating coil consisting of 36 twenty foot lengths of 4 inch pipe. The hot oil entered one end of a 30 inch expansion chamber from which the vapors passed to a dephlegmator. Here part was condensed and returned to the heating coil, and part passed on to a water cooled condenser. The residuum from the expansion chamber was drawn off continuously. The following tabulated data are given:

	Mexican Fuel Oil	Mid. Cont. Fuel Oil
Hours, fire to stream	3	4.5
Hours on stream	13	21.0
Pressure used	110	135
Total charge (gallons)	21,054	30,213
Pressure distillate	10,834	18,355
Per cent pressure distillate	51.5	60.7
Residuum (gallons)	7,906	10,348
Per cent residuum	37.6	34.2
Per cent gasoline (navy)	26.2	26.3
Baumé gravity	58.4	59.6
Oil-run (gal. per hour)	1,620	1,439
Pressure distillate (gal. per hour)	833	874
Gasoline (gal. per hour)	425	379
Carbon produced (tons)	5.9	2.8
Per cent carbon (by weight)	6.7	2.4

[41] U. S. Pat. 1,123,502, Jan. 5, 1915. (Application filed Nov. 20, 1909.)
[42] See *Bull. 16*, Kansas City Testing Laboratory.

Gas-oil was also decomposed in a cracking unit consisting of a coil made from 48 twenty-foot lengths of 4 in. pipe. The diameter of the expansion chamber in this instance was 10 in. The pressure used was 135 lbs., running time 196½ to 203½ hours, per cent pressure distillate 62, per cent gasoline 35 to 40, per cent of carbon produced 0.5 to 1.1, and the Baume gravity of the gasoline 58.5. Detailed data are given for four runs in Bulletin No. 16 already referred to.

The Dubbs process is also described in the report of a committee of the Western Refiners Association.[43] The plant consists of 10 twenty-foot lengths of 4-in. extra-heavy pipe joined into a continuous coil by return bends, but made into two rows with six lengths of the 4 in. pipe in the lower row and four in the upper row. The entire coil is heated in a furnace held at a temperature of 1540° F. The hot oil discharges from the coil into an expansion chamber consisting of four 20-ft. lengths of 10-in. common extra-heavy pipe connected in series by return bends. These 10-in. pipes are set horizontally in a chamber and are not heated but are lagged to prevent excessive heat loss.

The oil is pumped into the 4-inch pipe-coil where it is heated to about 820° F. and then discharged into the expansion chamber. The 10-in. pipes are kept about one half full of oil. The vapors pass upward through goose-necks to a manifold thence through a spiral vapor condenser, and finally to a water-cooled condenser. A pressure of 135 lbs. is maintained throughout the apparatus. The residuum is continuously drawn from the 10-in. expansion chamber. The results of an 108-hour test run were as follows:

Gas oil treated (gallons)	20,952
Non-condensable gas formed (cu. ft.)	25,851
Fuel used was equivalent to 4,677 gallons of 14 Be. fuel oil.	
Products formed (given as per cents of oil charged):	
Gasoline, 58 to 59° Be., 430 end-point	26.3
Kerosene, 40 to 41° Be.	14.1
Pressure distillate bottoms, 31 to 32° Be.	27.2
Residuum, 13 to 14° Be.	24.7
Loss	7.7

Another patent[44] was issued to J. A. Dubbs in 1915, one[45] to L. A. Dubbs in 1919, and three[46] to a third member of the Dubbs family whose name alone breathes of cracking processes, Carbon P. Dubbs.

The Universal Oil Products Company owns a small but well equipped cracking plant at Riverside, Illinois, and the Roxana Petroleum Co. a small plant at Wood River, Illinois. The process has been licensed

[43] *Nat. Pet. News*, Sept. 24, 1919, 25-6.
[44] U. S. Patent 1,135,506, April 13, 1915, "Treatment of Petroleum."
[45] U. S. Patent 1,319,053, Oct. 21, 1919, "Process of Treating Hydrocarbon Oils."
[46] 1,231,509, June 26, 1917, "Method of Treating Petroleum and Other Hydrocarbons." 1,392,629, Oct. 4, 1921, "Process of Converting Hydrocarbons." 1,411,961, Apr. 4, 1922, "Process of Treating Oils."

to the Schaffer Oil and Refining Co., the Moore Refining Co., the Associated Oil Co. of California, and the Continental Oil Co.[47]

The "Tube-and-Tank" Process of the Standard Oil Company of New Jersey.

The Standard Oil Company of New Jersey has developed a process called the "Tube and Tank" process. It is based at least in part on patents issued to Carleton Ellis.[47a] A recent statement by Frank A. Howard[47b] presents the general features of the process.

The oil is heated to 750° F. to 850° F. by passage through 130 4-in. tubes set in a suitable furnace. The tubes discharge into a pressure-still 6 ft. in diameter and 40 ft. long that is set in the furnace above the tubes. The steel walls of this vessel are 1¾ to 2 in. thick. A pressure of 250 to 350 lbs. per square inch is held on the pressure-still or reaction chamber. The pressure relief valve is located at the end of the reaction-chamber opposite that at which the heated oil enters.

The process is claimed to be better than that of Burton. The Standard Oil Company of New Jersey is building the "tube and tank" units for its own use, and is licensing the process to others. The equipment is said by Mr. Howard to cost between $80,000 and $110,000 per each 1000-barrel charging capacity, the variation in cost presumably depending on salvage of existent equipment. A Burton plant is said to cost $250,000 per 1000-barrel charging capacity. Not only is the initial investment less if the "tube and tank" process is used, but the royalty is only 10¢ per barrel of oil charged, as compared to the royalty of 16⅔¢ per barrel charged by the Standard Oil Co. of Indiana for the Burton license.

The "tube-and-tank" process is the basis of the infringement suit brought by the Standard Oil Co. of New Jersey against the Pure Oil Company, on account of the use of the Cross process by the latter. The answer[47c] of the Pure Oil Company denies the alleged infringement, and includes numerous citations of patents and technical articles to show that the patents of Ellis covered points that had long been known.

The Lewis Process.

The Lewis process is a pressure still process in use by the Atlantic Refining Company. It is covered by U. S. Patent 1,364,443. A recent letter from Dr. Delbridge to the *Petroleum Refiner* indicates that the quantity of gasoline made is sufficient to warrant including this process among the important cracking processes.

[47] *Nat. Pet. News*, Nov. 29, 1922, 26-7.
[47a] U. S. Patents: 1,249,278, 1,396,999, 1,415,232 and possibly others issued to Ellis.
[47b] *Nat. Pet. News*, Nov. 22, 1922, 17-18.
[47c] *Nat. Pet. News*, Sept. 13, 1922, 19-21.

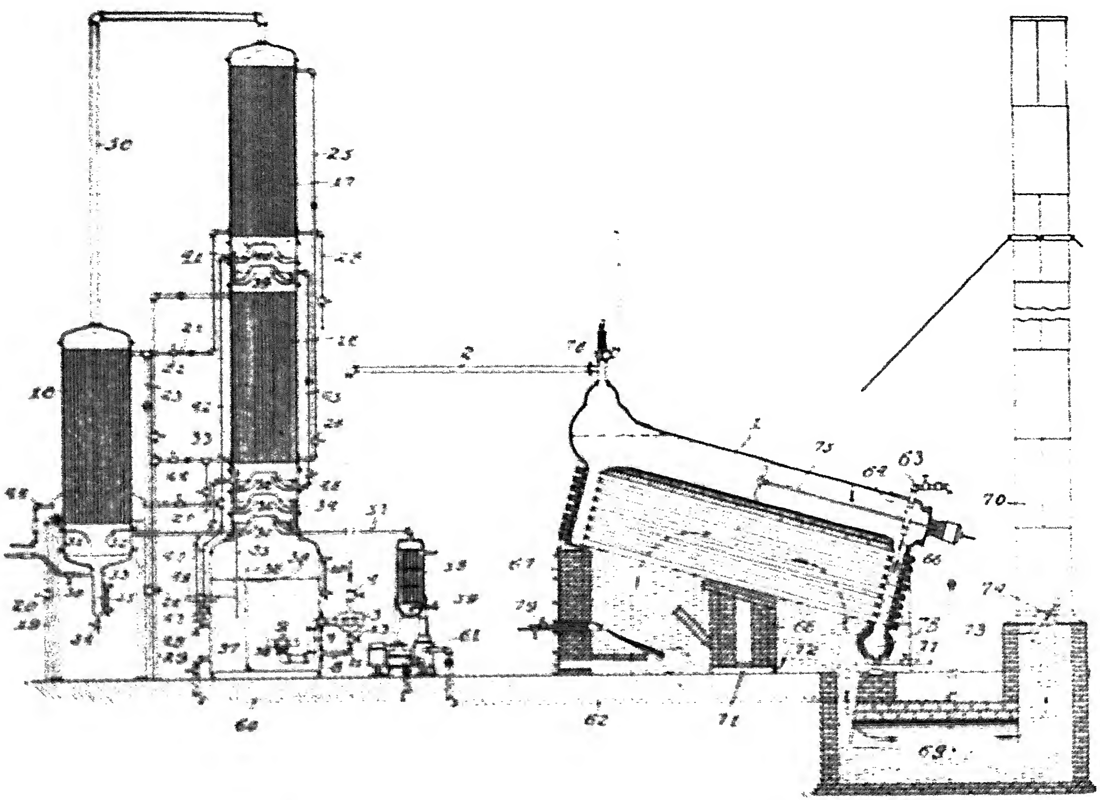


FIG. 120.—Diagram of Emerson "Impact System."

The Emerson Process.

The Emerson process [48] is the invention of Mr. V. L. Emerson, and is referred to by the S. S. E. Co. of Philadelphia as the "Impact System." The apparatus is shown diagrammatically in Figure 120, taken from U. S. Patent No. 1,367,807. It consists of a small pressure-still of the Heine-boiler type operated in conjunction with the "impact" injectors, tubular partial condensers, and tubular final condenser. The raw-material enters the tank "8" shown beneath the partial condenser. The reflux condensate also enters this chamber. Hot vapors from the pressure-still are expanded through valve "4" into the impact device. This consists of a pair of opposed nozzles so arranged that they function as injectors. The expanded gas as well as oil drawn by the injectors from tank "8" are thus commingled and the liquid atomized or broken into the finest particles by what is called "attritive" effect of the kinetic energy of the gas. It is claimed that the kinetic energy is here converted to other forms of energy, probably in part electrical, that serves to dissociate and decompose the large hydrocarbon molecules. Hence the name the impact process.

The mixture of gas and hydrocarbon mist is forced into the liquid in tank "8" so that its heat content is utilized in heating and in distilling the lower boiling fraction of this liquid. The vapors from tank "8" pass through the partial condenser where the heavier portions are condensed, and the naphtha passes to the condenser "18." Liquid from tank "8" is pumped to the pressure-still where it is introduced through a series of jets that are immersed in the liquid. The purpose of this procedure is to "deliver the oil with great velocity downwardly into the passages between the partitions of the rear header, thereby producing a rapid circulation of the oil undergoing distillation."

For a discussion of the theory of the process, reference should be made to the patent specifications and to an article by L. S. Paddock.[49]

The Gulf Refining Company has installed twelve Emerson stills with the accessory equipment. The drum and tubes of a still hold about 20 barrels of oil. The pressure used is 125 lbs., and the temperature 700 to 750° F. A run lasts about 36 hours, but cooling and cleaning increases the time for a complete cycle to 55 hours. One barrel of 50 to 52° Bé. naphtha is produced per hour during the 36 hour running period. Upon distillation the naphtha yields 70 per cent of 56° Bé. gasoline.

[48] U. S. Patents: 1,337,831, Apr. 20, 1920, "Apparatus for Distillation" 1,346,797, July 13, 1920, "Apparatus for the Conversion of Hydrocarbon Oils." 1,346,798, July 13, 1920, "Process for the Conversion of Hydrocarbon Oils." 1,352,255, Sept. 7, 1920, "Safety Damper for Oil-Stills and the Like." 1,350,057, Oct. 19, 1920, "Apparatus for Distillation or the Like." 1,367,806, Feb. 8, 1921, "Apparatus for the Conversion of Hydrocarbon Oils." 1,367,807, Feb. 8, 1921, "Process for the Conversion of Hydrocarbon Oils." 1,414,000, May 2, 1922, "Process for the Conversion of Hydrocarbon Oils."

[49] *Pet. Age*, Mar. 1, 1922, 22.

The following notes are quoted from the article already referred to in the *Petroleum Age*.

"George F. Benhoff, formerly of the Pierce Oil Corporation, says:

"'The Emerson impact process will produce as a minimum 1000 barrels of commercial gasoline per unit per month, with an initial boiling point below 125° F. and an end point below 437° F.

"'The apparatus can be operated if so desired to produce only enough residue to operate the plant. From numerous experimental runs it was decided that 65 per cent of the total oil processed is the ideal quantity of commercial gasoline to run for.

"'By allowing ten days each month for cleaning, repairs and any other delays you might incur in operating the stills, it would allow twenty working days at 50 barrels per day or 1000 barrels per month per unit.'"

The cost of a single unit is estimated as $45,000 and that of the accessory tankage, pumps, fittings and so on as $15,000.

In the same article E. A. McCadden of the Pure Oil Company is quoted as follows:

"My purpose is to set before the reader a plain statement of facts deduced from the actual operation, conducted on a commercial unit of the Emerson Impact Process, with sufficient details to enable anyone with a knowledge of refining operations and costs to determine the value of the Emerson Process to their individual needs.

"As conditions vary in different localities the writer deems it wise to confine his statement to the details of yields of marketable materials obtained from the steam still distillation of the naphtha distillate obtained from the Impact Process together with the amount of fuel consumed and estimated cost per barrel for labor. All other charges for the finishing of the material into marketable products can best be supplied by interested parties.

"The time required for operation from 'fire started' to 'fire drawn' was 40 hours and 35 minutes. Three hours and 5 minutes were required to bring the still over. Sixteen hours, after the fires are drawn, is allowed for cooling, cleaning, etc.

"The material used for this test was standard white distillate of gravity 44.1 Bé.

Standard white distillate consumed	5831 Gallons
Naphtha distillate produced	5196 "
Fuel oil consumed	1588 "

"The estimated labor cost to produce one barrel of naphtha distillate is 24 cents. The per cent of naphtha distillate produced was 89.11, gravity 53.0, initial point 103 and end point 510. A steam distillation of the naphtha distillate yielded 65 per cent of gasoline, gravity 55.6, initial point 118, end point 44.7.

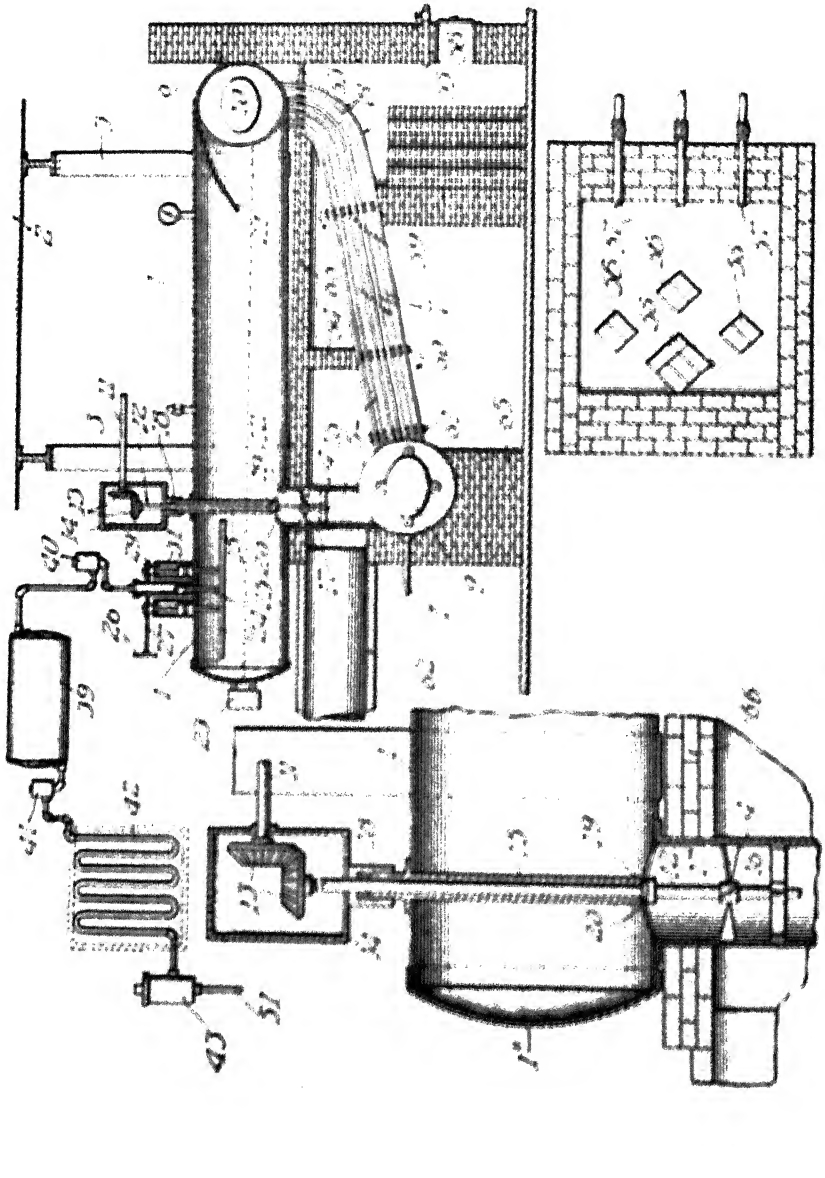


FIG. 121.—Jenkins' Still

"A summary of yields based on the run of standard white distillate through the Impact Process is as follows:

	%	I. P.	E. P.	Grav.
Gasoline	57.92	118° F.	417° F.	55.6
			Flash	Fire
Steam still bottoms	27.62	100° F.	220° F.	42.8
Tar	5.60	(Fuel oil)		
Loss	8.77	(All distillations)		

"On re-running the steam still bottoms through the Impact Process it has been determined that the per cent yield of gasoline to be obtained from them will fully equal the per cent yield obtained from the original charging stock of standard white distillate."

The fuel consumption of 1588 gallons to cracked 5831 gallons of S. W. distillate should be particularly noted. It amounts to slightly over 27 per cent of the raw material treated. This is a very heavy fuel consumption.

The Jenkins Process.

The Jenkins process [50] is the invention of Ulysses S. Jenkins. Gas-oil or other similar distillate is introduced into the tubular pressure-still shown in Figure 121. A propeller is used to better the circulation of the oil that would normally result from heating the oil in the inclined tubes. Vapors from the still pass through the pressure-relief valve "40" before entering the condenser.

The still is fired from a Dutch oven, and the hot gases directed past the 2½-inch tubes by baffle-walls. Oil is pumped to the still and vapors are withdrawn continuously throughout the operating period. It has been found safe and practical to pump a total volume of oil to the still equal to fourteen times the charging capacity of the still. The still is cooled by drawing the fire and circulating charging-oil. The following data covering the cracking of a pressure-still gas-oil (this oil had been through the process once) are given by Mr. Jenkins.[51]

The pressure used was 105 to 110 lbs., and temperature 700 to 710° F.

Total oil circulated	17,130 gal.
Cracked-distillate produced	11,600 "
Natural gas used as fuel	48,000 cu. ft.

[50] U. S. Patents: 1,226,526, May 15, 1917, "Method of Obtaining Gasoline and Other Light Oils from Heavier Hydrocarbons." 1,247,883, Nov. 27, 1917, "Method of Treating Heavier Hydrocarbons" (issued to S. Schwartz). 1,321,749, Nov. 11, 1919, "Apparatus for Treating Petroleum Products."

[51] *Chem. Met. Eng.*, 23 (1920), 911.

Products—calculated as per cents of oil charged:

	Per Cent
Gasoline (118° F. initial, 460 end-point)	24
Kerosene	29
Steam-still bottoms	14
Pressure-still bottoms	27
Loss	6

Data covering another run are also given by Mr. Jenkins.[52]

Time required for heating-up and running	56½ hours
Total gas-oil of 33.4° Bé. charged	44,467 gallons
Natural gas used as fuel at 2½ pounds pressure (1000 B.t.u. per cu. ft.)	175,975 cu. ft.

Products:

	Per Cent
Gasoline, 56 to 58° Bé., 130 initial 450 end-point	29.2
Naphtha, 48° Bé., 470 end-point	9.1
Kerosene distillate 39.4° Bé.	32.0
Gas-oil 35° Bé.	3.7
Pressure-still bottoms 24° to 26° Bé.	20.7
Coke	1.5
Gas and loss	3.8

W. C. Black, President of the Jenkins Process Company of Chicago, states[53] that the special feature of the Jenkins process is the rapid transfer of heat to the oil, and the consequent large charging capacity in a given time. According to Mr. Black, a batch charge of 250 barrels is run in 48 hours in an ordinary pressure-still, whereas the Jenkins still of 235 barrel batch charging capacity, when operated in the usual semi-continuous fashion, will handle 1000 barrels of gas-oil in 24 hours, and will continue to operate at this rate until it is necessarily cooled for cleaning. Ten Jenkins stills can be counted on to run at least 5,000 barrels of gas-oil per day whereas it would require 50 ordinary pressure-stills to handle this quantity of oil. He also calls attention to the fact that the Jenkins still may be used for topping, in which event the daily capacity would be 3,000 barrels or more of crude-oil.

The Jenkins Petroleum Process Company, on January 25, 1921, filed a bill of complaint in the United States Court, District of Maine, against the Sinclair Refining Company alleging that the Isom process of this company is the invention of U. S. Jenkins. The suit is not based on infringement of patent rights, but on a previously made contract.[54]

[52] *Chem. Met. Eng.*, 23 (1920), 524.
[53] *Pet. Mag.*, Feb., 1921, 80.
[54] *Nat. Pet. News*, Feb. 9, 1921, 24.

The Jenkins process is used by the Moore Refining Company of Arkansas City, the Allied Refining Company of Okmulgee, and the Lakeside Petroleum Company of Augusta.

The Isom Process.

The Isom process used by the Sinclair Refining Company is the invention of Edward W. Isom.[55] Gas oil or other similar distillate is heated under pressure in a still of special design. The products are condensed under pressure also.

All the heating takes place in vertical tubes through which the oil is circulated as a result of the heating and also by a propeller placed in the supply pipe outside the furnace. The vertical heating tubes are connected outside the furnace by suitable manifolds. The hot oil leaving the tubes circulates to a still or reaction chamber that is partly filled with the hot liquid. The lighter hydrocarbons volatilize here and pass through a dephlegmator to the condenser. It is claimed that little carbon deposits on the heating tubes on account of the rapid circulation of the oil, and also because the tubes are vertical.

I regret to say that I have no data covering the results obtained by the operation of this process. However, as stated in the patent, the invention "relates more particularly to the means for heating the oil." It is probable that the yield and quality of the product are comparable to those of other pressure-still processes.

Bacon-Brooks-Clark Process.

This process is covered by several U. S. Patents [56] assigned to the Gulf Refining Company. The oil is heated under pressures of 100 to 300 lbs., and at temperatures between 350 to 500° C., in vertical pipes 6 to 18 in. in diameter and 20 ft. long. The aim is to have as large a ratio of heating surface to volume as possible. A large vessel is connected to the bottom of the vertical pipe. It is intended that the carbon shall collect in this, and shall be drawn off from time to time. Oil enters and vapor leaves from the top of the cracking tubes.

The following yields of 56° Bé. gasoline are claimed:[57]

	Per Cent
Oklahoma gas-oil (32° Bé.)	45
Mexican fuel-oil (12° Bé.)	50
California fuel-oil (14° Bé.)	47
Caddo heavy crude (12-14° Bé.)	48

[55] U. S. Patent 1,285,200, Nov. 19, 1918, "Art of Cracking Hydrocarbons."
[56] U. S. Patents: 1,101,482, June 23, 1914, "Treatment of Petroleum Hydrocarbons." 1,131,309, Mar. 9, 1915, "Manufacture of Gasoline." 1,334,731, Mar. "Apparatus for the Manufacture of Gasoline."
[57] *News*, Apr. 14, 1920, 30-32. *Chem. Met. Eng.*, 23 (1920), 911.

The Coast-Cosden Process.

The cracking processes in use by Cosden and Company are covered by many patents [*] issued to J. W. Coast and to J. S. Cosden.

These patents cover pressure still operation and construction with particular reference to avoidance of the deposition of carbon on the still bottom. The use of steam in the dome of a pressure still, and various methods of utilizing the heat in the hot vapors are also covered. It is quite without the scope of this book to discuss the numerous patents in detail. The reader is referred to the specifications.

The first Coast stills were built in 1917 at Tulsa. At present, I understand 100 Coast stills are operated by Cosden and Company, and 20 by the Producers and Refiners Corporation at Tulsa. The stills are 8 x 40 ft., and made of heavy plate. A scraper moves the deposited carbon to the rear of the still where it does no harm since it is beyond the heated portion of the still bottom. Vapor from the still passes to a tubular dephlegmator where the higher boiling part is condensed and returned to the still. The more volatil hydrocarbons pass through a valve that controls the reduction of the pressure from 95 lbs., the working pressure in the still, to atmospheric pressure. The vapors are condensed at atmospheric pressure. The yield of marketable gasoline is 30 to 35 per cent of the gas oil treated, or about the same as that of the Burton process.

[*] U. S. Patents: 1,250,798, Dec. 18, 1917, "Art of Distilling Hydrocarbons." 1,250,799, Dec. 18, 1917, "Art of Cracking Petroleum Hydrocarbons." 1,250,800, Dec. 18, 1917, "Apparatus for Cracking Petroleum Hydrocarbons." 1,250,801, Dec. 18, 1917, "Art of Cracking Petroleum Hydrocarbons." 1,252,401, Jan. 8, 1918, "Art of Distilling Hydrocarbons." 1,252,999, Jan. 8, 1918, "Art of Cracking Hydrocarbons." 1,253,000, Jan. 8, 1918, "Apparatus for Cracking Hydrocarbons." 1,258,190, Mar. 5, 1918, "Art of Cracking Hydrocarbons." 1,258,191, Mar. 5, 1918, "Means for Cracking Hydrocarbons." 1,258,196, Mar. 5, 1918, "Apparatus for Cracking Hydrocarbons." 1,261,215, Apr. 2, 1918, "Art of Cracking Petrol. Hydrocarbons." 1,291,414, Jan. 14, 1919, "Apparatus for Cracking Hydrocarbons." 1,307,724, June 24, 1919, "Apparatus for Cracking Hydrocarbons." 1,333,964, Mar. 16, 1920, "Art of Treating Hydrocarbons." 1,345,132, June 29, 1920, "Art of Treating Hydrocarbons." 1,345,133, June 29, 1920, "Apparatus for Cracking Hydrocarbons." 1,345,134, June 29, 1920, "Apparatus for Distilling Hydrocarbons." 1,348,264, Aug. 3, 1920, "Apparatus for Cracking Hydrocarbons." 1,348,265, Aug. 3, 1920, "Art of Cracking Hydrocarbons." 1,348,266, Aug. 3, 1920, "Art of Cracking Hydrocarbons." 1,348,267, Aug. 3, 1920, "Art of Cracking Hydrocarbons." 1,348,268, Aug. 3, 1920, "Apparatus for Cracking Hydrocarbons." 1,349,815, Aug. 17, 1920, "Apparatus for Cracking Hydrocarbons." 1,349,816, Aug. 17, 1920, "Art of Cracking Hydrocarbons." 1,349,817, Aug. 17, 1920, "Apparatus for Cracking Hydrocarbons." 1,353,316, Sept. 21, 1920, "Apparatus for Cracking Hydrocarbons." 1,355,311, Oct. 12, 1920, "Apparatus for Treating Hydrocarbons." 1,355,312, Oct. 12, 1920, "Art of Cracking Hydrocarbons." 1,370,881, Mar. 8, 1921, "Art of Cracking Hydrocarbons." 1,372,937, Mar. 29, 1921, "Apparatus for Cracking Hydrocarbons." 1,374,357, Apr. 12, 1921, "Apparatus for Treating Hydrocarbons." 1,379,333, May 24, 1921, "Art of Cracking Hydrocarbons." 1,398,629, Apr. 23, 1921, "Art of Cracking Hydrocarbons." 1,400,800, Dec. 20, 1921, "Art of Cracking Hydrocarbons."

The Coast-Improved Process.

The "Coast-Improved" process has recently been devised by Coast, and is now used by the Empire Refineries, Inc., at Okmulgee. The marketing of this process is in the hands of the F. W. Freeborn Engineering Corporation of Tulsa. The process is said to be capable of making 45 to 50 per cent of marketable gasoline, which is better than the results obtained by the Coast-Cosden process and other similar pressure-still methods.

The Muehl Process.

The Muehl process [58a] is a pressure-still process controlled by the recently organized Interstate Refineries, Inc. The oil, after passing through heat-exchangers and heater, enters the "primary reaction-chamber." This is a pressure-still fitted with a carbon-removing scraper that is drawn along the bottom of the still from front to rear, picked up and carried forward, and then drawn to the rear again. The still-bottom is not heated directly. The pressure used is 100 pounds, and the temperature about 750° F. According to its sponsors, this process has been successfully used in Kansas City since 1920, and other plants are now being built. It is claimed that the process handles either distillates or residuums.

The Aluminum Chloride Processes.

The aluminum chloride processes of George W. Gray [59] and Almer McDuffie McAfee [60] are those best known to the oil fraternity. The general theory of the use of $AlCl_3$ has been briefly reviewed in the preceding chapter. The modern processes are adaptations of that of Friedel and Crafts who took out an English patent in 1877. (B.P. 4769.)

Gray states in his first patent that the low boiling products formed when an heavy oil is treated with anhydrous aluminum chloride will be such as to have an end point approximately the same as the tem-

[58a] *Pet. Ref.*, Dec. 7, 1922.

[59] U. S. Patents: (Gray.) 1,193,540, Aug. 8, 1916, "Method for Converting Higher-boiling Petroleum Hydrocarbons into Lower-boiling Petrol. Hydrocarbons." 1,193,540, Aug. 8, 1916, "Method for Converting Higher-boiling Petroleum Hydrocarbons into Lower-boiling Petrol. Hydrocarbons."

[60] *J. Ind. Eng. Chem.*, 7 (1915), 737-41, and U. S. Patents: 1,127,465, Feb. 9, 1915, "Process of Improving Oils." (McAfee.) 1,099,096, June 2, 1914, "Manufacture of Aluminum Chloride." 1,144,304, June 22, 1915, "Manufacture of Aluminum Chloride." 1,202,081, Oct. 24, 1916, "Recovery of Aluminum Chloride." 1,206,874, Dec. 5, 1916, "Utilization of Aluminum Chloride Residues." 1,235,523, July 31, 1917, "Process of Treating Oils." 1,277,328, Aug. 27, 1918, "Process of Saturating Oils." 1,277,329, Aug. 27, 1918, "Purifying Oils." 1,277,-092, Aug. 27, 1918, "Process of Purifying Paraffin." 1,325,073, Dec. 23, 1919, "Manufacture of High-grade Low-boiling Petroleum Products." 1,326,072, Dec. 23, 1919, "Improving Oils." 1,326,073, Dec. 23, 1919, "Manufacture of High-grade Low-boiling Petroleum Products." 1,424,574, Aug. 1, 1922, "Process of Converting Oils."

perature at which the reaction between the oil and the $AlCl_3$ occurred. If one desires to operate at temperatures of 550 to 600° F. a dephlegmator must be used in order that the higher boiling hydrocarbons will be condensed and returned to the still.

McAfee emphasizes not only the conversion of high boiling hydrocarbons into lower-boiling hydrocarbons, but also the improvement in the quality of the oil residue in the reaction vessel.

Generally speaking the aluminum chloride process involves the addition of 5 to 8 per cent of anhydrous chloride to the heavy oil. The oil must be dry, and to ensure this it must be heated to 300 to 350° F. Should any water remain it hydrolyzes the aluminum chloride, liberating HCl and forming aluminum hydroxide. Upon addition of aluminum chloride to a light oil the oil becomes darker in color as the addition compounds are formed.

The mixture is heated to about 550° C., stirred and held at this temperature. The vapor that passes off is composed of a mixture of lower-boiling and higher boiling hydrocarbons, and also in part of compounds of $AlCl_3$ with the hydrocarbons. A partial condenser is used to condense all but the part of the desired volatility.

The quantity of aluminum chloride used, and the operating conditions are determined in each individual case, for no two oils are exactly the same. The gasoline produced is of the finest quality. The distillation curve is excellent, and the content of unsaturated hydrocarbons, sulfur, and oxygen compounds nil. After re-running the only refining treatment required is a wash with dilute caustic soda to remove the HCl, and a water wash.

The main drawback to the aluminum chloride process is the cost of the reagent. It is doubtful if any process of recovery would prove profitable, for it is inevitable that the $AlCl_3$ shall be very largely decomposed during the protracted distillation period. The heavy oils contain oxygen and sulfur compounds that decompose with formation of H_2O and H_2S. These react with the aluminum chloride forming HCl which passes off, and the hydroxide or hydrosulfide of aluminum which stays in the still. Also as the distillation proceeds substances rich in carbon, a granular coky mixture, separates and doubtless encloses some of the $AlCl_3$. As a result of the chemical changes and mechanical inclusion the distillation period is limited to 24 to 48 hours.

Gasoline yields varying from 15 to as much as 60 per cent can be obtained, depending on the nature of the heavy oil used, the operating conditions, and the quantity of $AlCl_3$ added. The residue in the still consists of a granular coke and a heavy oil that can be easily separated. This oil is of much better quality than the oil used as raw material, and can be worked up for lubricating oils, paraffin, and petroleum.

The granular coke is of little value because of the undecomposed chloride as well as other inorganic impurities. It really constitutes a waste and its production is one of the drawbacks to the process. The hydrochloric acid liberated is also a nuisance, since it rapidly corrodes metal apparatus wherever any water is present.

The aluminum chloride processes have not been used in a large way as yet, though the Gulf Refining Company at Port Arthur is still carrying on development work along this line under Dr. McAfee's direction, and the Texas Company is doing likewise with the Gray process.

Were it not for the cost of the aluminum chloride the McAfee and Gray processes would be widely used today because of the excellent quality of the product, and the avoidance of the use of pressure. On the basis of 60 lbs. of aluminum chloride for every 100 gallons of heavy oil the production of each gallon of gasoline must be charged with the cost of 1.0 to 1¼ lbs. of $AlCl_3$.

A process recently patented[61] by Dr. C. M. Alexander may have a direct bearing on the future of the aluminum chloride processes. The alumina or other aluminum containing material is mixed with the fuel and finely powdered. The mixture is injected into a gas tight furnace along with air and chlorine. I am informed by Dr. Alexander that the cost of 1 pound of $AlCl_3$ is about 3¢ if the operating unit is making 15,000 pounds per day.

The process of C. O. Hoover[62] has attracted some attention recently. A small plant has been operated at Fairmount, near Enid, Oklahoma.

A novel method of using aluminum chloride or ferric chloride is disclosed in the patent[63] of C. M. Alexander and G. H. Taber, Jr. The vapor of the heavy oil and of the anhydrous metal halide are mixed and passed through a heated reaction zone. The process may be styled a vapor-phase aluminum chloride process.

Leslie-Tunison Process.

Although I do not yet feel free to discuss the details of the cracking process that Mr. Tunison and I have jointly invented and developed, I cannot refrain from briefly mentioning several outstanding features or advantages.

1. Principles are involved that have not been appreciated or utilized heretofor, and upon the use of which we hope to obtain basic patent protection.

2. The heaviest fuel-oils and residuums are successfully handled with production of generous yields of gasoline.

3. No pressure is used. This greatly simplifies both design and operation, and eliminates the danger element inherent in the operation of pressure-still plants.

4. No chemicals are used.

5. Our process is not a competitor of either pressure-still or vapor-phase processes, but is adjunct to, and can be used with profit in conjunction with, these processes. At the same time that we produce

[61] U. S. Patent 1,366,626, Jan. 25, 1921, "Process of Making Metallic Halides."
[62] *Nat. Pet. News*, Apr. 26, 1922, 17, 20-21.
[63] U. S. Patent 1,381,098, June 14, 1921, "Process of Catalyzing Oil and Apparatus Therefor."

gasoline we make other distillates suitable for use as raw materials in other processes.

6. In many instances existent equipment can be utilized in practising our process if a very moderate expenditure is made for alterations and additions.

7. Our process is so simple that the ordinary still-man can be easily taught to handle the operation.

8. The cost of the required plant equipment is small, and the depreciation no more rapid than that of ordinary refinery equipment. No complicated high-temperature furnaces are required.

9. The throughput per unit time is large. This results in goodly capacity for a moderate investment, and reduces operating costs per unit of product.

10. The basic principles of our method can be applied to pressure-still plants with the result that operating-time is greatly reduced.

11. The product made by our process is highly satisfactory both as to boiling range and olefin content. It is easily refined by ordinary methods.

We do not regard the process as a panacea for all the ills of cracking plant technology, but do claim it to be a simple and effective procedure based on new principles, and that it can be profitably applied to the handling of the fuel-oils and residuums of the Mid-Continent, the Gulf Coast, California, and Mexico. A very large source of raw materials that have heretofore been unavailable for cracking is opened to the refiner. Some refiners are now running fuel-oils and residuums to coke, and cracking at least a part of the distillates thus produced. Our process accomplishes the production of these distillates more effectively than coking, and at the same time yields 20 per cent or more of gasoline. In addition to this, we find that by steam-reduction of the heavy distillates we can prepare lubricants of good quality from the heavy asphaltic oils, and that these oils do not require acid-treatment but simply filtration through fuller's earth to render them suitable for the market.

Other Cracking Processes.

A few cracking processes by virtue of inherent merit have been used widely enough to become well known. Others through discussion in the technical press, through advertising, or through the manner of their promotion have received much attention. But many more, either because the interests controlling them have not desired publicity, or because the processes have proved to be of little value are not widely known.

None of the processes claiming to bring about hydrogenation of the olefins have been successful. Likewise processes using fused baths such as molten lead, and the processes claiming the use of catalysts (with the exception of iron oxide, alumina, and aluminum chloride) have all been failures.

To be familiar with the details and the actual merit of all of the many processes that have been used would necessitate an acquaintance with what is going on behind a great many ten-foot board fences. The processes enumerated or commented on briefly in the following paragraphs are less widely known than those described in the foregoing pages. The list is doubtless incomplete. On the other hand many "processes" so-called are not worthy of the name. And yet "dark-horses" may appear to take their place in the activities that are slowly but surely changing refinery practice.

The Snelling Process.

The Snelling process [64] consists in heating the oil under pressure without removal of the products as formed. The volume of the chamber should be from two to ten times the volume of the oil treated. Pressures as high as 900 pounds are used. The Palmer process already referred to is somewhat similar. The difficulty with methods that do not remove the products continuously lies in the low yield per cycle, and the relatively long time required for cooling.

The Wells Process.

The first Wells plant [65] was built at the refinery of the Avis Refining Company of Jacksboro, Tennessee. The process has also been tried by Cosden and Company, and by the Constantin Refining Company of Tulsa.

The Conerty Process.

The Conerty pressure-still process is used by the Lincoln Refining Company of Robinson, Illinois, and the Independent Refining Company, and three other Pennsylvania refineries.

The Brownlee Process.

This process [66] is covered by U. S. Patents Nos. 1,308,161 of July 1, 1919, 1,320,376 of Nov. 4, 1919, and 1,325,927 of Dec. 23, 1919. It consists in heating a mixture of oil and gas in tubes that connect a series of drums. The process is controlled by the Benedum-Trees interests.

Hubbard Process.

The patent of Hubbard [67] covers the heating of heavy hydrocarbons under pressure, cooling under pressure, followed by distillation.

[64] *Bull. Am. Inst. Min. Eng.*, 1915, 695-704. *Am. Gas Lt. J.*, 102 (1915), 156.

[65] U. S. Patents: 1,232,454, July 3, 1917, "Process of Decomposing Oil." 1,248,225, Nov. 27, 1917, "Process of and Apparatus for Decomposing Hydrocarbons."

[66] *Nat. Pet. News*, 11 (1919), 35-6, 38, 40. *Pet. Age*, 6 (1919), 470.

[67] U. S. Patent 1,326,056, Dec. 23, 1919, "Process of Producing Low-boiling Hydrocarbons."

Cherry Process.[68]

This process is the invention of Dr. L. B. Cherry and consists in subjecting hydrocarbon vapors to the action of a temperature of 900° F., and at the same time to the influence of a high frequency, high voltage, oscillatory electric current, radiating from a fine wire held concentrically within the vertical cracking tube. So far as I am aware the process has never been successful commercially, although it attracted some attention.

Other Processes.

In addition to the foregoing the Hansen process has been used by the O. K. Refining Co., of Niotaze, Kansas; the Blaisdell process by the Mutual Oil Co. of Chanute; the Goebel process by the Kansas City Refining Co., Kansas City, Kansas; the Corey process by the Wright Producing and Refining Company, Cherryvale, Kansas; the Ormonde process by the Ætna Refining Co. of Louisville, Ky.; the Forward process by the Oil Refining and Development Company of Urbana, Ohio; the Landis process by the Augusta Refining Company of Augusta, Kansas, and the Duluth Refining Company of Sapulpa, Oklahoma; the Anderson process by the Great Western Refining Company of Erie, Kansas, and the Uncle Sam Oil Company of Cherryvale, Kansas, and Tulsa, Oklahoma; and the Wilkins process by the Sapulpa Refining Co. of Sapulpa, Oklahoma.[69]

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[68] *Trans. Am. Electrochem. Soc.*, 32 (1917), 297-316. *Pet. Mag.*, Mar., 1920, 58-64. U. S. Patents: 1,229,886, June 12, 1917. 1,327,023, Jan. 6, 1920. 1,345,431, July 6, 1920.
[69] See James, H. C., *Oil Gas J.*, 16 (1917), 20, 40-2; 21, 34-6; 22, 38-9, 46; 23, 38-9, 46; 24, 38-39. Also *Pet. Rev.*, 34 (1916), 69-70, 98.

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Chapter X.

The Chemical Treatment of Gasoline.

Gasoline as marketed today is usually refined by a treatment with sulfuric acid followed by neutralization with a solution of caustic soda. Much gasoline that is now refined could in all probability be used satisfactorily if it received no chemical treatment, but trade practice has established standards of color and odor that must be met, for business, if not for technical, reasons. On the other hand, the development and use of cracking processes has resulted in the production of "synthetic" gasolines that must be refined if they are to be satisfactorily utilized.

Since color and odor, and upon occasion, sulfur content and acidity, are the criteria, other than distillation range and gravity, by which the purchaser judges the quality of the product, the refiner must make passable gasoline even though he may know that a product somewhat off color and odor could be used with entire satisfaction. The intelligent purchaser may also be entirely aware of this fact, but will argue with truth that present standards of color and odor prevent the marketing of much carelessly refined gasoline. Prior to the advent of the cracking processes the chemical treatment of gasoline was regarded as a simple operation. Little difficulty was encountered in practice, except in refining distillates containing moderate to large amounts of sulfur, and as a consequence the chemistry of the process was not studied in detail. Our present limited knowledge of the fundamental chemistry of refining is adequate testimony of past neglect.

The extensive use of cracking processes, and the difficulties encountered in refining cracked products, has awakened interest in refining methods. The odor of good gasoline is no longer a definite thing, for gasolines produced by pressure-still processes and vapor-phase processes are possessed of odors quite distinctive. The old-line refinery worker is inclined to the belief that this adjective should be spelled without the "di"-, and with a "k" in place of the "c." Difficulty is found in some instances in so refining vapor-phase gasoline-stocks as to make a water-white product. The presence, in cracked gasolines, of unsaturated hydrocarbons of several types, introduces new difficulties in refining and in the subsequent steam-distillation. Gum deposition and oxidation have become factors to be taken into account.

As a consequence of producing gasoline from a great variety of crude petroleums, and by many thermal processes, diverse refining methods are in use. Straight-run distillates from the best crude oils require no treatment except re-running with steam. Some are washed with caustic soda solution or sodium plumbite solution, while others,

including all gasoline stocks made by cracking processes, are necessarily treated first with sulfuric acid and then with an alkaline wash, which is frequently sodium plumbite, followed by redistillation with steam.

The Cause of Color and Odor.

Little is known of the cause of the color of petroleum oils. The few colored hydrocarbons that are known, as, for example, members of the fulvene series, contain conjugated double-bonds. It is possible that the characteristic yellow color of the distillates produced by vapor-phase cracking may be attributable in part to di-olefin compounds. This is pure conjecture, for it has never been demonstrated. The darkening of petroleum distillates on exposure to the air, or to air and light, is a familiar phenomenon that suggests a connection between color and the presence of oxidized compounds. Sulfur and nitrogen compounds may also be responsible for coloration, either directly or as oxygen carriers.

The more volatil petroleum distillates often have pronounced and disagreeable odors. This is particularly true of the benzines produced by cracking processes. For the reason that these benzines are known to contain moderate to large proportions of olefin hydrocarbons the bad odor has frequently been attributed to the presence of the olefins. However, the odors of the pure mono-olefins are not more offensive than those of the paraffins or naphthenes. But the olefins with conjugated double bonds, such as cyclohexadiene, are possessed of sharp disagreeable odors, and may contribute in some measure to the odor of cracked gasolines. Upon standing, gasoline distillates, particularly cracked distillates, are oxidized, and a sharp odor develops. Samples of an unrefined vapor-phase cracked product that stood in my laboratory for two years showed this marked change in odor. They were contained in 1000 cc. glass-stoppered graduated cylinders, and were not exposed to the sunlight. At the same time a brown resinous substance separated and collected at the bottom of the cylinders. The volume of this viscous resinous material was 1.2 per cent of the volume of the distillate from which it separated.

The components, other than oxygen compounds, that are mainly responsible for the bad odor of gasoline stocks are sulfur compounds and nitrogen bases. Straight-run distillates contain nitrogen compounds in very small amount only, but distillates made by cracking processes contain larger quantities of nitrogen bases. When California residuum is cracked, ammonia is formed in moderate amount, though the predominant nitrogen compounds are derivatives of the tertiary bases pyridin and quinolin.

Reaction of Sulfuric Acid with the Substances Composing Gasoline.

Since sulfuric acid is so generally used to refine volatil distillates it is important to know as much as possible of its reactions with the impurities in, and the main components of, gasoline stocks. Present

knowledge of this subject is limited, both as a result of imperfect knowledge of the substances that compose light distillates as well as lack of information on the reaction of sulfuric acid with these compounds. Furthermore, physical as well as chemical changes, if one may draw a line here, may be of some importance. Also two types of chemical change that are not discussed in the text books may be involved. For example, a large number of chemical compounds of the "-onium" type are possible when substances that contain oxygen, sulfur, and nitrogen atoms in their molecules are brought together under suitable conditions. A vast but scattered chemical literature exists that treats of the reactions of substances containing atoms of several valencies, but, for lack of correlation and "boiled-down" presentation, is not as yet available as a useful working tool. The book "Chemical Reactions" by Dr. Falk should be consulted as it is the most concise treatment of the subject now in print. Professor J. M. Nelson of Columbia University has presented a most illuminating course of lectures on this general subject for several years. It is to be hoped that these may in time be available in printed form.

1. *Reaction with the paraffins and naphthenes.*

If one consults the text books of organic chemistry the statement is found that the paraffins do not react with concentrated sulfuric acid at ordinary temperatures. Probably this is true. Brooks and Humphreys [1] found that pure normal heptane was unaffected by 48 hours shaking with 1.84 sp. gr. sulfuric acid at 25° C. The same was true of di-isopropyl. I have found that gasoline and kerosene from paraffin-base crude oil, when treated with successive portions of sulfuric acid of any strength less than 100 per cent H_2SO_4 by weight, showed no volumetric loss, but when treated with fuming sulfuric acid of 6 per cent or of 12 per cent excess SO_3 showed a volumetric loss. A single treatment with a large excess of 12 per cent excess SO_3 sulfuric acid occasioned a loss of 10 per cent by volume of a paraffin-base distillate, and over 35 per cent of a mixed-base distillate.

Brooks and Humphreys found that di-isopropyl lost 32.2 per cent of its volume to fuming sulfuric acid of 15 per cent excess SO_3 when agitated with this reagent for 35 minutes at 22° C. Other observers have found that the higher paraffins in natural gas are removed, at least in part, by fuming sulfuric acid. Gurwitsch [2] found that paraffins and naphthenes are apparently absorbed by concentrated sulfuric acid when they are mixed with other substances that react with sulfuric acid. The exact nature of the phenomenon is yet to be explained.

However all this may be, it appears that since the impurities in crude benzines are so much more reactive toward sulfuric acid than the paraffins or naphthenes, since the sulfuric acid used in refining gasoline stocks is ordinary 66° Bé. acid, and since the acid is seldom used in amounts exceeding 3 lbs. per barrel of distillate treated, the

[1] *J. Am. Chem. Soc.*, 40 (1918), 847-8.
[2] Wissenschaftliche Grundlagen der Erdöl bearbeitung.

probability is that the loss of paraffins and naphthenes is small indeed.

2. *Reaction with aromatic hydrocarbons.*

Aromatic hydrocarbons are present in small quantities in the volatil distillates of asphalt- and mixed-base crude oils. The lower molecular weight aromatic hydrocarbons are not sulfonated by cold concentrated sulfuric acid. Brooks and Humphreys [3] state that the higher aromatic homologs are readily sulfonated. If fuming sulfuric acid is used at ordinary temperatures the aromatic hydrocarbons are readily sulfonated.

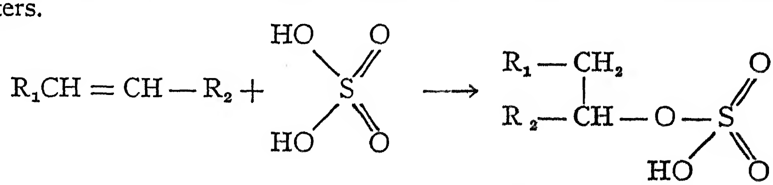
3. *Reaction with the olefin hydrocarbons.*

The reaction of sulfuric acid of various strength with the olefin hydrocarbons is a subject of the greatest importance, for these substances are present in moderate to large amount in all distillates produced by cracking processes. It is not safe to base general statements on the reactions of a few olefins, as is shown by the work of Brooks and Humphreys.[4] Olefins are not completely removed from distillates by polymerization to "tars" or by formation of "sulpho-acids" as has been believed by some. The use of sulfuric acid as a reagent in determining "unsaturation" has possibly contributed to the erroneous belief that olefins react in some quantitative manner with sulfuric acid.

When the mono-olefins are treated with sulfuric acid at least four reactions are possible. The extent to which each occurs depends upon the nature of the olefin, the strength of the sulfuric acid, the temperature, the time allowed, and the manner in which hydrocarbon and acid are mixed.

a. *Formation of alkyl esters.*

The olefin may react with sulfuric acid to form mono- and di-alkyl esters.

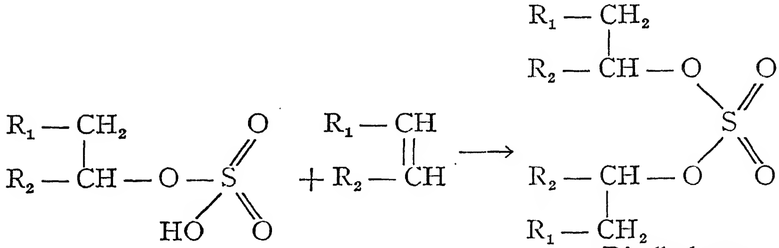


Mono-alkyl ester

The mono-alkyl esters are soluble in water, but not soluble in petroleum distillates. They are not quickly hydrolyzed when mixed with water at ordinary temperature, but of course hydrolyze yielding secondary alcohol if the temperature of the aqueous reaction mixture is allowed to rise.

The mono-alkyl esters will react with more olefin to form di-alkyl esters:

[3] *J. Am. Chem. Soc.*, 40 (1918), 848.
[4] *Ibid.*, 822-56.



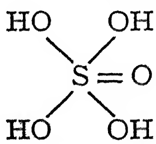
Di-alkyl ester

The di-alkyl esters unfortunately are soluble in petroleum distillates, and are not removed by the soda treatment. They introduce one of the difficulties in refining olefinic distillates. When the treated distillate containing these substances is distilled they decompose with liberation of SO_2. This decomposition can be minimized, and the difficulty eliminated, by lowering the temperature of distillation through the introduction of steam. Wet steam rather than superheated steam should of course be used. The esters will hydrolyze, at least in part, to form the acid mono-ester or sulfuric acid. This accounts for the corrosion that has been noted in fire-and-steam- or steam-stills used for re-running treated cracked-distillates. A little caustic-soda solution introduced into the still is effective in preventing this corrosion.

b. *Formation of Alcohols.*

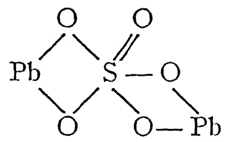
When some olefins are treated with sulfuric acid, and the reaction mixture then poured into cracked ice, a yellowish oil separates that is mainly composed of secondary or tertiary alcohols. It has been believed by some that these are formed by hydrolysis of the alkyl-sulfuric acid esters, but the work of Brooks and Humphreys shows that this is not the case. The separation of the alcohol mixture is immediate, whereas the hydrolysis of the alkyl-sulfuric esters is inappreciable in 10 minutes even at 90° C. The only measurement of the rate of hydrolysis of alkyl-sulfuric esters that has come to my attention is that of Linhart,[5] who showed that a dilute solution of ethyl sodium sulfate was only 16 per cent hydrolyzed when heated to 60° C. for eight days.

Brooks and Humphreys suggest that the alcohols may be formed by hydrolysis of the esters of ortho-sulfuric acid:



Esters of this acid would doubtless differ in stability and rate of hydrolysis from those of sulfuric acid. Esters of ortho-sulfuric acid

[5] *Am. J. Sci.*, 35 (1913), 283.

have not been isolated, but basic sulfates such as 

have been regarded as derived from it. The exponents of the "onium" compound theories would doubtless be able to offer an explanation of the formation of these alcohols. In any event it is certain that the free alcohol is not present in the olefin-acid reaction mixture, for none of it can be obtained by shaking this mixture with an immiscible solvent.

The alcohols are not appreciably soluble in the hydrocarbon distillates. The characteristic odors of refined cracked distillates are probably in some measure the result of the presence of alcohols.

The formation of alcohols is dependent in large measure on the strength of the sulfuric acid used, as well as upon the nature of the olefin. Acids of 80 to 90 per cent strength favor alcohol formation. When acid of 100 per cent H_2SO_4 is used alcohol formation is nil.

c. *Formation of polymers.*

Contrary to common belief the mono-olefins are not polymerized to tars by sulfuric acid. Brooks and Humphreys have found that the formation of di-polymers predominates, but that tri-polymers and possibly higher polymers are formed. These substances after distillation are water-white liquids. The di-polymer of β-methyl-β-undecene was water-white even before distillation. The polymers formed from the mono-olefins are straight-chain compounds with one double bond. They are not of cyclic structure. Their reactivity with sulfuric acid is less than that of the olefin from which they were formed. They are soluble in the hydrocarbon distillates, and do not enter the sludge. The presence of these compounds, along with the di-alkyl sulfuric acid esters, explains the increase in specific gravity and the broadening of the distillation range of treated cracked-distillate as compared to that of the raw benzine. These effects are not marked in refinery practice where but 2 to 3 lbs. of acid is used to refine a barrel of benzine, but are very noticeable if the benzine is treated with an excess of acid in the laboratory.

The tars that are formed when olefinic distillates are treated with sulfuric acid are polymerized di-olefins. The di-olefin hydrocarbons are the really objectionable hydrocarbon impurity in cracked-gasolines. They oxidize readily, thus causing the development of sharp odors. Presumably they are responsible for the formation of gummy and resinous substances that separate from raw or poorly refined cracked-gasolines on standing. Fortunately, on account of the reactivity of the di-olefins, they are effectively removed by treatment with sulfuric acid, and the refined products so made are entirely satisfactory. Distillates produced by vapor-phase cracking methods contain more di-olefins than those made by other processes.

d. *Oxidation.*

The refining of cracked oils, particularly those distillates made by vapor-phase processes, is attended by the evolution of sulfur dioxide. This shows that the sulfuric acid is oxidizing some of the hydrocarbons, and is itself reduced. If the difficulty is serious it may be largely avoided by the use of 80 to 85 per cent sulfuric acid, at least for the "water-acid" and the next addition of acid.

In connection with the foregoing discussion, as well as with that which follows, a review of Brooks and Humphreys' experiments with individual olefins will be found of interest and importance. Table LX presents a summary of their work.

TABLE LX

SUMMARY OF BROOKS AND HUMPHREYS' WORK

Olefin	Treatment	Result and Product
β-methyl-α-butene, b. p. 33-35° C.	Dissolved in 2 vols. of 85% sulfuric acid at 10° C.	Tertiary alcohol, 45% of theoretical yield. No polymers.
β-methyl-α-pentene, b. p. 64-66° C.	Treated with 2 vols. 85% sulfuric acid at 10° C. Only 12 g. of the hexene available.	55% dissolved. Tertiary alcohol formed.
α-hexene, b. p. 60.5-61.5° C.	52 g. slowly added to 100 cc. 85% sulfuric acid at 15° C. during interval of 20 minutes.	The hydrocarbon dissolved completely. Hexyl sulfuric acid. Secondary hexyl alcohol.
Iso-α-heptene, b. p. 85-86° C.	15 g. treated with 25 g. 85% sulfuric acid.	7.3 g. polymers—mostly dipolymer of b. p. 220-224° C.
γ-heptene, b. p. 93-95° C.	68 g. added during 30 minutes to 200 g. 85% sulfuric acid at 15° C.	Olefin dissolved completely. Yielded heptyl sulfuric acid and the alcohol.
γ-ethyl-β-pentene, b. p. 97-98° C.	To 102 g. of the olefin 120 g. of 1.84 sp. gr. sulfuric acid were added at 0° C.	Formed and tertiary alcohol and the alkyl sulfuric acid.
Tetra methylethylene, b.p. 73-74° C.	46.5 g. of the olefin were added to 150 g. of 85% sulfuric acid at 0° C. in one hour.	Dissolved rapidly. 37.6 g. dipolymer, 1.6 g. of the alcohol, and alkyl ester corresponding to 7.1 g. of the olefin were formed.
Hexene mixture, b. p. 58-70° C., made from the monochlor hexanes obtained by chlorinating a hexane fraction from petroleum.	70 g. of the hexene mixture slowly added at —10° C. to 100% sulfuric acid.	62 g. polymers formed. No alcohols. Small amount alkyl sulfuric acid. Oxidation occurred, for SO_2 was evolved.

(*Continued on next page*)

TABLE LX—(*Continued*)

Olefin	Treatment	Result and Product
α-octene, b. p. 122-124° C.	To 52 cc. of the octene 50 cc. of 85% H_2SO_4 were added at 20° C.	Little discoloration and little heat. 38 cc. of an oil layer formed that blackened and evolved SO_2 with violence when distilled.
	30 cc. octene treated with 96% sulfuric acid.	Yielded 74% polymers.
α-iso-octene, b. p. 111-112° C.	60 g. olefin slowly treated with 225 g. 85% sulfuric acid at 15° C.	9 g. secondary alcohol 25 g. dipolymer 13.8 g. higher polymers some unchanged octene.
β-methyl-β-undecene, b. p. 210-211.5° C. at 752 mm.	79 g. olefin treated slowly with 130 g. of 85% sulfuric acid at 20° C.	Formed straw colored layer and 75.5 g. of a viscous water-white oil layer. The oil was almost entirely di-polymer.
	Treated with 1.84 sp. gr. sulfuric acid.	Results practically the same as with 85% sulfuric acid.
Hexadecene (from spermaceti), b. p. 130-150° C.	Treated with 85% sulfuric acid.	Olefin remains practically unchanged.
	Treated with 1.84 sp. gr. sulfuric acid.	25% unchanged olefin, 52.4% dipolymers, 22.6% viscous higher polymers.
Menthene, b. p. 169-170° C.	119 cc. olefin treated with 100 cc. 85% sulfuric acid.	101 cc. supernatant oil was composed of 35% unchanged menthene and 55% di-menthene. 12.5 g. menthol separated from the acid layer.
Methyl Δ_1-cyclo-hexene, b. p. 105-6° C.	15.6 g. olefin treated with 35 g. 85% sulfuric acid at 0° C.	11.5 g. polymers that were mostly di-polymers. 4.0 g. hexanol.
α-pinene, b. p. 155°-159° C.	79 g. olefin treated with 150 g. 85% sulfuric acid at 0° C.	Mainly di-polymer and the viscous tri-polymer.
β-pinene.	Treated with 85% sulfuric acid at 0° C.	Mainly di-polymer and viscous tripolymers.
Limonene.	Treated with 85% sulfuric acid at 0° C.	Mainly polymers.
Myrcene, b. p. 165°-167° C.	Treated with 85% sulfuric acid at 0° C.	Reaction so vigorous that tar formation and carbonization could not be prevented.

The experiments of Brooks and Humphreys confirm the belief of Michael and Brunel [5a] that the tendency of straight-chain olefins to form alcohols and alkyl sulfuric acid esters decreases with increasing molecular weight. The amylenes and hexenes are most reactive in this respect.

With regard to the effect of constitution of the olefins on reactivity Brooks and Humphreys make the following statement:

"The substitution for the hydrogen of ethylene groups, which impart a strongly electro-negative character, results in decreased reactivity to sulfuric acid. Thus we find that cinnamic and fumaric acids are not appreciably acted on by 95 per cent sulfuric acid at ordinary temperatures; and similarly dichloroethylene is acted upon only very slowly under the same conditions. Allyl bromide is also more stable toward concentrated sulfuric acid than is propylene. On the other hand we find that tetramethyl ethylene is more reactive toward the acid than its isomer, α-hexene, which finds an explanation in the fact that the unsaturated group $> C = C <$ in α-hexene has three of its valences taken up by hydrogen, while in tetramethyl ethylene these are replaced by the more strongly electropositive methyl groups. From this standpoint the greater reactivity of amylene, butylene, and propylene as compared with ethylene is also readily explained. The behavior of the olefins of still greater molecular weight, however, is difficult to explain. Why they should be quite stable, as compared with the amylenes and hexenes, is not apparent, nor has any explanation suggested itself to us as to why γ-ethyl-β-pentene should yield 72 per cent alcohol and 12 per cent polymers, and α-methyl-β-undecene 97 per cent polymers and only a trace of alcohol, since their structures are quite similar."

Brooks and Humphreys observe that the tendency to polymerize increases with increasing molecular weight.

4. *Compounds Containing Oxygen.*

Naphthenic acids, if present, are effectively removed by treatment with sulfuric acid. This was first pointed out by Zaloziecki,[6] and confirmed by Gurwitsch [7] who showed that these substances were found in sludge in far greater proportion than would be expected if their removal was merely a question of solubility and partition between two immiscible solvents. E. Pyhala [8] also had isolated naphthenic acids from the acid sludges obtained when Russian kerosene distillates were treated with 94 per cent sulfuric acid. Mabery [9] states that the naphthenic acids such as $C_6H_{11}COOH$ are responsible for the ready formation of emulsions in the washing of lubricating oils with caustic soda. He states further that the smallest excess of soda must be avoided in washing the acid treated oils for the sodium salts of the naphthenic acids

J., 41 (1909), 118.
5 (1892), 905.
87 (1914), 323.
506-7.
(1916), 522.

have a marked emulsifying effect. J. Kendall and C. D. Carpenter[10] have shown by cryoscopic methods that aliphatic and aromatic acids, ketones, aldehydes and phenols form oxonium addition compounds with sulfuric acid.

Naphthenic acids are not present in American oils in as large amount as in Russian oils, nor are they all mal-odorous. Brooks and Humphreys isolated naphthenic acids from the gasoline fraction of a Mexican petroleum that smelled like the Russian acids, but obtained acids from a Texas oil that were viscous and nearly odorless.

The lower boiling naphthenic acids are derivatives of cyclo-pentane,[11] such as 1-methyl-2-carboxy cyclo-pentane.

5. *Nitrogen Compounds.*

The nitrogen compounds are present in the lighter straight-run petroleum distillates in very small amounts. However, distillates made by cracking heavy California or Mexican residuums contain sufficient quantities of nitrogen compounds to cause most disagreeable odors. So far as is known, the nitrogen containing substances are tertiary bases such as alkylated pyridines and quinolines. As would be expected they are effectively removed by treatment with sulfuric acid, presumably as "onium" compounds. Pyhala[12] states that the nitrogen compounds are the impurities that are acted upon first by sulfuric acid.

6. *Sulfur Compounds.*

Sulfur present as H_2S, or in compounds that readily dissociate or decompose to give H_2S as one of the products, is readily removed by sulfuric acid. The reaction between concentrated sulfuric acid and H_2S is an oxidation-reduction:

$$H_2S + H_2SO_4 \longrightarrow SO_2 + S + 2H_2O$$

The nature of the sulfur compounds in petroleum oils has been studied in a few instances only. The papers of Mabery on American and Canadian oils, and the review of F. M. Perkin[13] with the accompanying discussion, are the most valuable contributions to the literature of this subject.[14] The effect of sulfuric acid on the alkyl sulfides found by Mabery in Canadian oils, on the thiophenes found in small quantities in Russian and German oils, and on the thiophanes found by Mabery in Canadian petroleum, has not been studied in great detail, yet we are not without some pertinent information. Mabery, referring to the thiophanes, says,[15] "Since the sulfur compounds described in this paper,

[10] *J. Am. Chem. Soc.*, 36 (1914), 2498-2517.

[11] See Bushong, F. W., *Pet. Mag.*, May (1921), 162. Markownikow, *Ann.*, 307 (1899), 367. Aschan's "Chemie der Alicyclischen Verbindungen" (1905), 508. Also *Ber.*, 24 (1891), 2710.

[12] *Pet.*, 9 (1914), 1506-7.

[13] *J. Inst. Pet. Tech.*, 3 (1917), 226-50.

[14] See Chap. II for a discussion of the sulfur compds. of petroleum.

[15] *Proc. Am. Ac. Arts & Sci.*, 41 (1905), 113.

as well as the alkyl sulfides, are also readily soluble in sulfuric acid, they should be removed as a part of the sludge in refining burning-oil distillates."

N. A. Anfilogoff[16] states that the thiophanes are readily "soluble" in sulfuric acid, and are the most easily removed sulfur compounds. The alkyl hydrosulfides, thioalcohols, or mercaptans are more troublesome to remove. They are found in large quantity, according to Anfilogoff, in Canadian, Mexican, Texan, Persian and Egyptian oils. These compounds react with metallic oxides such as mixed iron and cupric oxides. A third and more troublesome group are the thioethers or di-alkyl sulfides. These are not affected by sulfuric acid or metallic oxides. The most difficult to remove of all the sulfur compounds are the alkyl disulfides. They may be reduced to mercaptans, preferably by the action of zinc and NaOH, and the mercaptans afterward removed by the use of metallic oxides.

While Anfilogoff's statements sound very well because they have the beauty of definiteness, it should be noted that they were presented in discussion only, and were not accompanied by the evidence of experimental results. His statements do not agree with the conclusions of Dr. Thole, mentioned below.

Because of the fact that sulfur in combination is known to form sulfonium-addition compounds it is reasonable to expect that the sulfur compounds of the several known types would react readily with sulfuric acid. To what extent the presence of large quantities of olefinic hydrocarbons of several types alters the reaction tendencies is yet to be determined.

The effect of reagents on the sulfur compounds of a fraction up to 150° C. from Persian oil has been studied by Thole.[17] The total sulfur content was 0.11 per cent. Shaking with caustic soda solution reduced the sulfur content to 0.09 per cent. The sulfur removed was largely in the form of mercaptans, as was shown by acidifying the caustic soda extract and noting the odor of the small amount of oily liquid obtained. The distillate was then treated with concentrated sulfuric acid, whereupon the sulfur content fell to 0.03 per cent. Part of the sulfur so removed was present in the form of alkyl sulfides. The action of 95 per cent sulfuric acid on methyl and ethyl sulfides was studied, and it was found that these substances dissolved readily in the acid. The sulfur compounds that composed the remaining 0.03 per cent were not identified. Thole believes they may be thiophanes or more probably alkyl disulfides. The disulfides are not affected by strong sulfuric acid or by sodium plumbite.

Note should be taken of the fact that it is possible, by treating olefinic distillates with sulfuric acid, to increase rather than diminish ...r content. This is the result of the formation of di-alkyl ... esters that dissolve in the treated oil.

...and large, however, it is true that the sulfur content

...ch., 3 (1917), 243-5.

of the volatil distillates is reduced sufficiently by treatment with sulfuric acid and soda or sodium plumbite to produce satisfactory products. This was not true of distillates made years ago from Canadian and Lima oils, and a special technology that will be briefly referred to below was developed to remove the sulfur from these distillates. The fields from which these oils are obtained are of minor importance today.

Strength and Quality of the Sulfuric Acid Used in Refining.

The question of the proper strength of sulfuric acid for refining is of special importance in the treatment of the benzines produced by cracking processes, particularly vapor-phase cracking processes. Each distillate, in some measure at least, presents an individual problem. So far as the impurities are concerned there is no special reason why the usual 66° Bé. acid should not be satisfactory, but the presence of large quantities of olefins puts a different face on the matter. It is desired to remove impurities, but at the same time to avoid, (1) polymerizing the mono-olefins, (2) formation of dialkyl sulfuric acid esters, (3) oxidation.

Brooks and Humphreys[18] in discussing the refining of cracked gasolines state that "Sweet, stable gasolines may be made by treating with a small quantity, not over 6 per cent by weight of 85 to 90 per cent sulfuric acid, followed by washing with alkali in the usual manner and redistilling." Six per cent of sulfuric acid is equivalent to about 16 pounds per barrel and is much more acid than is required. Two to six pounds per barrel should be quite enough, even for highly unsaturated distillates. If difficulty is encountered with six pounds of acid per barrel of oil it will be well to look into the operation of the cracking plant rather than to try to get around difficulties in treating. My experience with regard to acid strength led me, some years ago, to the same conclusion that Brooks and Humphreys have expressed in their paper. Acid of 85 to 90 per cent strength—preferably 87 to 88 per cent—causes less polymerization and oxidation than stronger acid, yet is strong enough to polymerize the diolefins and to react with the oxygen, nitrogen, and sulfur compounds. The formation of di-alkyl sulfuric acid esters cannot be entirely avoided. It is less with the acid of less strength. The remedy comes in properly conducting the subsequent steam distillation. The temperature of the treated oil should be kept as low as possible during distillation. This requires that wet and not superheated steam be used.[19]

C. I. Robinson has patented[20] a process for the refining of Lima burning oils that involves the use of 98 per cent sulfuric acid at temperatures below 60° F. The sulfur compounds are claimed to be effectively removed.

[18] *J. Am. Chem. Soc.*, 40 (1918), 852.
[19] See discussion of steam distillation in Chapter V.
[20] U. S. Patent 910,584, Jan. 26, 1909.

F. Schulz [21] states that N_2O_3, N_2O_5 or SeO_2 when present in sulfuric acid cause a yellow color in the refined oils. Tests for these impurities in sulfuric acid are given. Refineries have rejected acid containing 0.02 to 0.04 per cent N_2O_3.

Kharitchkoff [22] also states that 0.05 to 0.07 per cent of N_2O_3 is the maximum percentage permissible in sulfuric acid to be used for refining.

On the other hand, Knotlenbelt [23] uses oxides of nitrogen in refining benzines, and claims to obtain a good product. Also F. C. Ruff [24] uses 66° Bé. sulfuric acid containing 0.25 to 0.75 per cent nitric acid in refining unsaturated distillates. The evidence as to the bad effects of nitrogen oxides is not conclusive enough to condemn the use of chamber acid in refining.

Special Considerations in the Refining of Cracked Distillates.

The refining of distillates produced by cracking processes has been referred to several times in the foregoing paragraphs, and the statements made need not be repeated here. However, several points of interest have not been mentioned.

A not uncommon practice is to mix the cracked distillates with straight-run distillates, and to treat the blend with acid. This practice is regarded as a makeshift by some, but in my opinion it is commendable. The rise in temperature resulting from the reaction of the sulfuric acid and olefins is greatly reduced and oxidation and polymerization are minimized.

One of the most important factors in the successful refining of olefinic distillates is the manner of bringing the distillate in contact with the sulfuric acid. It is desired to bring about reactions between the acid and the oxygen, nitrogen, sulfur, and diolefin compounds. This must be done in the presence of a large quantity of substances such as the mono-olefins that are reactive, but which must be affected to the least possible extent. Clearly the proper method is continuously to bring measured quantities of distillate and reagent into intimate contact for a brief period under carefully controlled conditions. The ordinary agitator is not a suitable apparatus for the accomplishing of this result. The process and apparatus patented by Dr. C. M. Alexander,[25] and used by the Gulf Refining Company is a good example of the application of correct principles. The distillate and acid are mechanically agitated as they flow through a conduit, the temperature of which can be controlled. The method and apparatus patented [26] by me, and assigned to the General Petroleum Corporation of California, is intended to bring about intimate contact, and thus to allow of the use of a minimum quantity of acid. Other patented processes that

tt.-*Harz.-Ind.*, 20 (1913), 82-4.
Vestsch., 6 (1905), 119.
Pet., 6 (1910), 196.
pr. 16, 1918.
an. 10, 1922.
uly 15, 1919.

have the same end in view are those of A. B. Foster,[27] Wilbur C. Laird[28] and H. T. Maitland.[29]

The Addition of Sulfuric Acid in Several Portions.

If the ordinary type of agitator is used in treating, the addition of the acid in three or more portions will be found advantageous. The drying of the distillate by the first portion of the acid, or "water-acid" as it is often called, is not so essential as when heavier oils are being refined. But the use of successive portions will better effect the desired result of removing small amounts of impurities, without at the same time reacting excessively with the mono-olefins, than if all the acid is added at once. The principle involved is much the same as that applied in washing precipitates in the laboratory. The sludge should be completely drawn after each addition of acid. The method is a none too good substitute for the scheme of treatment just referred to in which measured quantities of acid and distillates are intimately contacted in a special apparatus.

The Effect of Temperature and Time.

The refining of distillates other than those that are highly olefinic is easily carried out at ordinary temperatures. On the other hand, olefinic distillates react with sulfuric acid with liberation of heat. If the temperature is allowed to rise, oxidation will be excessive and other undesirable changes occur. It is possible that artificial cooling might be justified in some instances, but I am of the opinion that should such measures prove to be necessary the cracking plant rather than the treating plant should receive the extra effort and attention.

Dilution with straight-run distillate or the inclusion of kerosene distillate—even though this is a cracked distillate—is effective in preventing rise of temperature because of the heat capacity of the added distillate. The higher olefins contained in a cracked kerosene distillate are not so reactive as the lower molecular weight olefins in the cracked benzine.

If a continuous treating method is practised, water cooling can be used as a cheap and effective means of controlling temperature.

Time, as such, is really not a factor in treating operations in so far as the chemical changes per se are concerned. The reaction between acid and impurities is very rapid. But treating consists in bringing about a reaction between two immiscible liquids, and the time element is introduced as a result of this physical factor. The more intimate the mixing the shorter the time required. As has already been pointed out, the ideal scheme of reaction is one that gives the most intimate mixing. The time required is then a matter of seconds.

[27] U. S. Patent 1,394,486, October 18, 1921.
[28] U. S. Patent 1,320,396, Nov. 4, 1919.
[29] U. S. Patent 1,272,979, July 16, 1918.

The Alkaline and Water Wash.

Following treatment with sulfuric acid the distillate is washed with water—usually by spraying the water from perforated pipes above the surface of the distillate—to remove the larger part of the sulfuric acid, acid alkyl sulfates, and sulfurous acids that remain in the distillate after the sludge has been allowed to settle. The use of water allows of the use of less alkali in the subsequent wash with sodium carbonate, caustic soda, or sodium plumbite.

Those distillates that do not contain undue quantities of sulfur are then washed with a 10 per cent solution of sodium carbonate or sodium hydroxide. Experience determines the quantity of this reagent that must be used. An excess of soda may cause the formation of emulsions if the distillate treated is a highly olefinic one produced by a vapor-phase cracking process. Sodium hydroxide is more commonly used as a reagent than sodium carbonate. High grade caustic should be used, and purchased on the basis of actual content of NaOH. In grading commercial caustic the designations refer to content of Na_2O regardless of whether the sodium is present as NaOH, NaCl, Na_2SO_4, or other sodium compound.

If the distillate originally contained much sulfur it may advantageously be washed with "doctor" solution. This is prepared by dissolving litharge in caustic soda solution of 10 to 20° Bé. strength.

$$PbO + 2NaOH \leftrightarrows Na_2\ PbO_2 + H_2O$$

An excess of litharge is frequently used along with the sodium plumbite. All litharges are not equally satisfactory for preparing plumbite solutions. The reason is probably to be found in the physical state of the oxide, and possibly in part in the varying content of lead oxides other than the monoxide.

The combination of the sulfur compounds with the lead is aided by the addition of finely divided free sulfur. I have never heard a satisfactory explanation of the effect of free sulfur as used in this way. After a sufficient time of contact the plumbite reagent is drawn off and the treated solution washed with water. It is then ready for the steam-distillation.

In recent years straight-run distillates that are of good color, and that do not contain large amounts of sulfur, are refined by agitating with sodium plumbite followed by a water-wash and steam-distillation.

The doctor-solution does not react with all forms of sulfur. Hydrogen sulfide is easily removed as lead sulfide. Mercaptans form lead mercaptids and are also sufficiently acidic to combine with caustic soda. The sodium salts of weak acids of this nature are hydrolyzed so largely that sodium hydroxide is not an effective reagent for the removal of these compounds. The di-alkyl sulfides, the di-sulfides, the thiophenes, and the thiophanes are probably unaffected by sodium plumbite.

An article on the principles of the doctor treatment has been written

by S. Schwartz and H. G. Nevitt.[30] It is there stated that 30° Bé. NaOH solution dissolves about 3 per cent PbO, and that theoretically 0.6 gallons of this solution are required for every 0.01 per cent S in one barrel of oil. A refining treatment in which three times the theoretical requirement of doctor-solution is used is recommended.

Special Methods for the Removal of Sulfur.

The discovery of the Canadian and Lima oils that contained large quantities of sulfur in the burning-oil distillates led to the development of special methods for handling these oils. Numerous patents were issued, but a process said to have originated in Canada, but usually attributed to Frash, was most widely used and became best known.[31]

This process consisted in heating the distillate over finely ground cupric oxide in a 1200 to 1500 barrel still of the cheese-box type, fitted with an agitator framed from a central vertical gear driven shaft and carrying drag chains. The inside of the still was perfectly smooth so that the copper oxide could be kept in motion at all points, thus avoiding burning it onto the plates of the still. The oil was pumped to the still along with the copper oxide in suspension in a small amount of heavy oil. Five to six pounds of copper oxide were ordinarily used per barrel of oil. In refining some oils as much as twelve pounds of the oxide were used per barrel of oil treated. When about 85 per cent of the oil had been distilled, a second charge, along with more copper oxide in the proportion of 5 to 6 pounds per barrel of oil, was pumped in and mixed with the hot residuum. The agitator ran constantly. Six or seven charges of oil and oxide were run in this manner and then the fire was drawn and the still cleaned. The copper oxide was then withdrawn, cooled, filtered and the press-cake revivified by roasting. The sweetened water-white distillate that might still contain over 0.1 per cent sulfur could then be finished by the usual acid and soda treatment. The sulfur content of the completely refined oil would be about 0.04 per cent. The oil adhering to the cake furnished most of the fuel required. In the preliminary roasting, the sulfur content of the press-cake was reduced from 11 per cent to 3 or 4 per cent. The lumps were then crushed and passed through a series of roasting furnaces in which the sulfur content was reduced to about 1.5 per cent. After being ground to a fine powder, the oxide was ready to be used again.

Mixtures of copper oxide with lead monoxide and iron oxide have been used in methods similar to that of Frash, but in general copper oxide was cheapest and most satisfactory.

The Pitt process was also used to remove sulfur. It consisted in passing the oil vapor through a "filter" containing iron oxide heated to a fairly high temperature. The sulfur was effectively removed by this process, but the general scheme was not as easily handled or as cheap as the Frash method, and passed into disuse.

[30] *Pet.*, 7 (1919), 23, 96, 98, 100, 102.
[31] Mabery, *J. Am. Chem. Soc.*, 28 (1906), 422-3.

Another early method that was fairly successful was that of H. W. G. Kittredge, who operated a refinery near Petrolia, Ontario. In place of a plumbite solution, he used plumbite solution containing a large excess of litharge in suspension. After thorough agitation with this mixture, the oil was distilled. The condensate when treated with sulfuric acid and caustic soda, followed by a treatment with "doctor" solution, contained less than 0.06 per cent sulfur. The oil "broke" easily in the final treatment with "doctor" solution. The Kittredge method was quite successful in handling oils containing 0.4 to 0.5 per cent of sulfur, but was not so satisfactory in treating those of higher sulfur content.

A. D. Smith [31a] cites the following data as typical of the operations of the Kittredge method:

	Per Cent Sulfur
Sour Distillate, 45° Bé.:	
First run	0.30
Acid treated	0.25
Neutralized and washed	0.24
Lead saturated	0.24
Sweet Distillate, 47° Bé.:	
80% re-run	0.11
Acid treated and washed	0.045
Finished water-white oil	0.037

Brooks [32] calls attention to the fact that olefinic distillates that have been treated with alkaline plumbite, or thoroughly desulfurized by copper oxide, lose their strong unpleasant odor. He has found metallic sodium still more effective in producing a gasoline of good odor. Cracked gasolines treated with metallic sodium were found to retain their water-white color and good odor longer than straight-run products refined in the ordinary way with acid and soda. Brooks attributes this to the removal of sulfur compounds that, if allowed to remain in the gasoline, catalyze a process of auto-oxidation that is productive of compounds of sharp disagreeable odor such as formaldehyde, formic acid, fatty acids, and other oxygen compounds.

A. E. Dunstan [32a] and B. T. Brooks state that the Frash process does not remove the sulfur compounds from Mexican petroleum products, and also comment on the limited applicability of the alkaline plumbite solutions. They state, however, that their method of refining with dilute hypochlorite solutions is successful in desulfurizing gasolines and kerosenes from all types of crudes. The refined products do not contain chlorine. If the sulfur compounds are to be completely removed from a Persian gasoline, one pound of chlorine is required for 50 gallons of the gasoline. However, if it is only desired to refine to such an

[31a] *Nat. Pet. News*, Dec. 8, 1920, 89-93.
[32] *J. Fr. Inst.*, 180 (1915), 658.
[32a] *J. Ind. Eng. Chem.*, 14 (1922), 1112-4.

extent that the gasoline will pass the copper corrosion test and the "doctor" test, one pound of chlorine is sufficient to treat 333 to 500 gallons of gasoline.

The active agent in refining with chlorine is hypochlorous acid, an energetic oxidizing agent. Dunstan and Brooks recommend the use of liquid chlorine dissolved in water to make a solution containing 12 to 15 grams of available chlorine per liter. The sulfur compounds in the oil are oxidized fairly rapidly, and part of the oxidation products are water soluble. For instance, in refining gasoline from Persian petroleum, two hours was found to be a sufficient time. The hypochlorous acid solution and distillate were brought into contact by circulating the solution through centrifugal pumps that discharged the solution below the surface of the distillate. Pumps and agitators were iron or steel. It is claimed that these were not seriously corroded. According to Dunstan and Brooks, the best procedure is to refine a distillate composed of the gasoline and kerosene, and then to separate the gasoline by steam-distillation and filter the kerosene residue through dehydrated bauxite or other effective adsorbent to remove any slight coloration. The oxidized sulfur compounds are much more readily removed by bauxite than the original sulfur compounds. The loss in the entire operation is about 0.5 per cent when Persian distillate is treated in the manner just described. This compares to a loss of 3.0 per cent when this same distillate was refined with sulfuric acid.

The spent aqueous reagent is a 1 per cent solution of sodium or calcium chloride, and can be easily disposed of without creating a nuisance.

Treatment of Persian Distillate.

Once run naphtha

Sp. gr.	0.750
Sulfur	0.15 per cent
Color	P. W.

Agitate with a hypochlorite solution 12 g. available chlorine per liter

↓

Soda Wash

↓

Redistil

↓

Finished benzene

Sp. gr.	0.720
Sulfur	$<$0.01 per cent
Chlorine	$<$0.01 per cent

Residue

Filter through floridin or bauxite

↓

Finished kerosene

Sulfur	0.06-0.10 per cent
Chlorine	$<$0.01 per cent
Color	W. W.
Sp. gr.	0.790

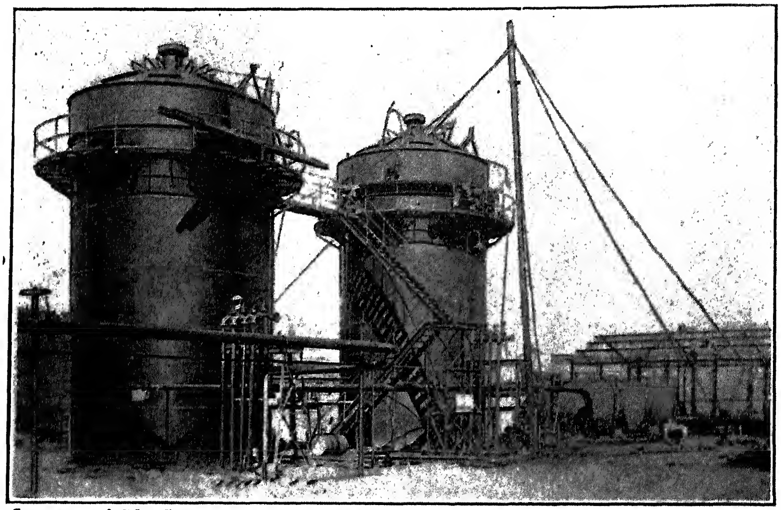
When gasoline only is to be treated, the filtering operation may, of course, be dispensed with. The purification treatment given above is so effective that with gasoline from Persian oil, containing the percentage of sulfur indicated, the regular commercial output passed the following tests:

(1)—100 cc. gasoline + 1 cc. $KMnO_4$ (0.1 N soln.) + 2 cc. 10 per cent sulfuric acid, and vigorously shaken, retains the permanganate color for 10 min., usually much longer.

(2)—When a sample of the gasoline is treated with sodium and alcohol, and, after the reaction is over, slightly acidified and tested with lead acetate, no film of lead sulfide can be detected.

(3)—The copper dish test is entirely negative.

(4)—The Doctor test is negative.



Courtesy of The Petroleum Iron Works.

FIG. 122.—Agitators.

Equipment Used in Chemical Treatment.

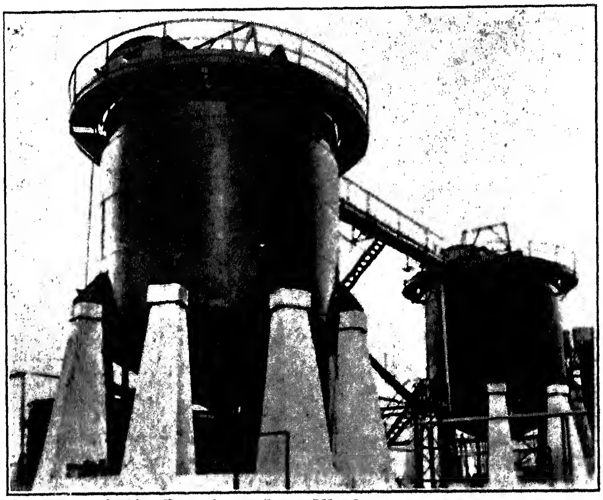
he Agitator.

The commonest apparatus used in the refining of distillates is the agitator. This is a cylindrical, lead-lined, sheet-steel, cone-bottomed tank of capacities ranging from a few hundred barrels up to 5000 barrels. The rivets of the shell are countersunk so that the inside of the tank presents a smooth surface for the lead lining. The lining of the vertical side wall is 8 to 10 pound chemical or antimonial sheet-lead supported from the top, and in the larger agitators also supported in the middle. The lining of the cone consists of several segments of 10 to 12 pound lead joined with a 4- to 6-inch lap. The lower ends of these sheets are burned to a circular sheet that in turn is burned to

the cylindrical lining of the outlet nozzle. The lining of the nozzle is flanged over the outlet fitting.

The agitator is supported either by continuing the plate-steel of the sidewalls down to the reinforced concrete foundation, or by columns of steel, cast-iron, or reinforced concrete. The latter method is much to be preferred in my opinion, because it avoids the nearly closed space beneath the agitator, and because in case of fire the columns will not buckle as will a wall of steel-plate. The probable extent of the damage in the event of an agitator fire is far less if the supporting structure remains intact.

The coned bottom of the larger sized agitators should be supported by columns or framing. The roof of the smaller agitators is often



Courtesy of The Petroleum Iron Works.

FIG. 123.—Agitators Supported by Columns.

hemispherical. The larger sizes are provided with flatter, but self-supporting roofs. The roof of the agitator, and in some types the upper portion of the vertical side wall, should be provided with explosion doors or hatches of ample size. These are often made too small, although it is far better to err in the opposite direction.

A pair of agitators of the skirted type is shown in Figure 122, and of the column-supported type in Figure 123. The general nature of stairways, walkways, and piping can be seen in these cuts.

Provision should be made for introducing the distillate, drawing the sludge and the washings, and drawing the treated distillate from the bottom of the cone. Acid and alkali are usually moved by means of a blow-case, and introduced through pipes entering the agitator above the oil. Compressed air is introduced through a pipe that projects well down into the cone. Wash water is introduced by means of a

system of perforated pipes or sprays located above the level of the distillate when the agitator is full. If the reagent is mixed with the oil, and circulated by means of a centrifugal pump, provision must be made for the necessary pipe-lines.

In using the agitator it should be filled as completely as possible with distillate, for this leaves a minimum space above the distillate to contain inflammable or explosive mixtures of vapor and air. The extent of the probable damage from an explosion is thus lessened. This point should be kept in mind in designing an agitator.

Each distillate presents its individual problems in treatment, and definite rules cannot be laid down. In general, the less the time of blowing with air the better. Excessive use of air results in unnecessary loss of the most volatil component and in treating some cracked distillates may cause oxidation.

Agitator Fires.

Ignition of the mixture of air and vapor above the distillate in the agitator may be caused by discharge of static electricity, by heat liberated in chemical action, or by sparks struck as a result of moving mechanism. Static charges may be caused by the movement of fluids in pumps or in pipes discharging into the agitator. They are most likely to be formed in dry cold weather. To avoid difficulty, all pipe-lines should be grounded to a water line, or to a plate several square feet in area, buried in moist earth.

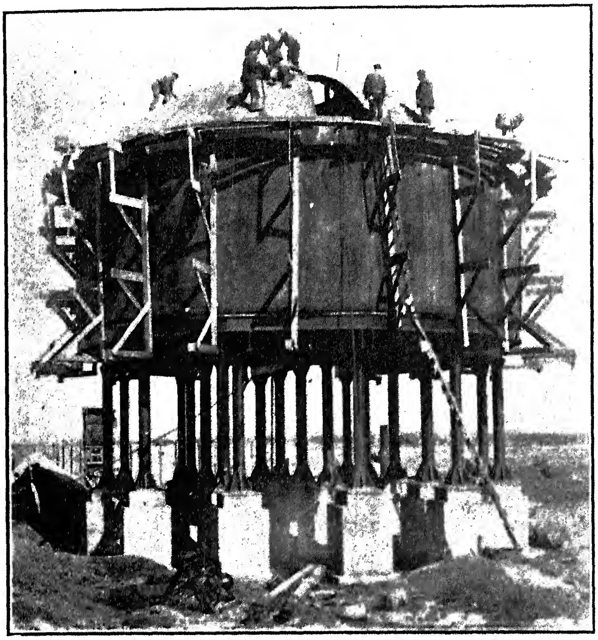
Chemical ignition is usually attributed to the formation of ferrous sulfide that is oxidized to ferrous and ferric sulfates with liberation of heat. Reactions of H_2S and SO_2 with liberation of sulfur that may combine with the iron of the agitator roof are possible. The actual cause of the difficulty is not well understood, but various preventive measures are taken. All surfaces may be covered with lead, which is not so reactive as iron. Protective paints are a none too certain remedy. Venting of the vapors above the oil, and the introduction of steam in the space above the distillate, are measures that may be employed with some benefit. Wooden roofs are not justified because of the fire risk. If used they should not be put together with iron nails.

Although the information may not be pertinent to the subject under discussion, it is of interest to note that Macadam[33] found that paraffin oils attacked lead and zinc with some readiness, but that tin and iron were not affected. Some oils were found to be worse than others. Engler[34] repeated Macadam's experiments and discovered that the metals were not attacked if air was excluded. It is possible that air used in agitation may be responsible for agitator fires, and that the use of an inert gas, such as washed flue-gas of low oxygen content, would eliminate difficulties.

An agitator should always be provided with a foam mixing-head for

[33] *J. Chem. Soc.*, 34 (1878), 355.
[34] *Ber.*, 12 (1879), 2186.

the introduction of carbon dioxide froth. Provision may also be made to draw the oil from the agitator rapidly. If the oil is pumped from the bottom the level of the burning liquid is lowered and the effect of the fire is not confined to the upper part of the agitator. To avoid this, a large pipe, open at the top and discharging to a tank, may be placed within the distillate when the agitator is full. Water may then be pumped into the agitator beneath the distillate, thus displacing the latter and confining the damage from the fire to the upper part of the



Courtesy of The Petroleum Iron Works.

FIG. 124.—A 2000-Ton Sulfuric Acid Tank Under Construction.

agitator. The use of effective foam-systems has, however, largely obviated the necessity of fire-protection measures of this sort.

Storage and Handling of Chemicals.

Sulfuric acid of 60° Bé. or greater strength can be safely stored in tanks constructed of mild steel or wrought iron. An acid storage tank should be well made and calked inside and out in order to avoid even small leaks. The tank should be supported by columns or other structural work in such a manner that all parts of the tank can be inspected easily. At least two manheads should be provided. All

flanges should be of pressed steel. Two acid-proof cocks of approved make should be used on the outlet line. These cocks should be turned at least once a day, whether acid is drawn from the tank or not, in order to prevent sticking. A very satisfactory cock is the Merril Company's lubricated Nordstrom plug valve. A 2000-ton acid tank, under construction, is shown in Figure 124.

Caustic-soda or soda-ash should be stored in a dry place. At some points a solution of caustic soda can be purchased to advantage and is convenient because it avoids handling the solids in order to get them in solution. The alkaline solutions are stored and handled in apparatus made from mild steel or wrought iron.

Continuous Treating Plants.

In recent years may refineries have adopted methods of continuous or semi-continuous treatment for the lighter distillates. The methods of Alexander and of Leslie already referred to are of this type. The plant of the Standard Oil Company of New Jersey is described by A. D. Smith[35] and need not be redescribed here. Important advantages, secured in some measure by most of these processes, are quicker and more intimate mixing of acid and distillate, better control of operating conditions, less loss by volatilization as the agitation is usually obtained by mechanical means and not by the use of compressed air, and larger capacity for a given investment and expenditure for operation.

Some distillates produced by cracking processes are not readily handled in a continuous treating plant, but results with most distillates are quite satisfactory.

Miscellaneous Refining Methods.

Liquid Sulfur Dioxide.

Edeleanu[36] has patented a process for refining burning oils in which the cooled oil is treated with liquid sulfur dioxide. The unsaturated and aromatic hydrocarbons, at temperatures below 0° C., are dissolved by this reagent while the paraffins and naphthenes are unaffected. The use of sulfur dioxide gas in refining is the basis of two patents issued to John C. Black.[37] According to Thole,[38] carbon disulfide, di-ethyl sulfide, mercaptans and ethyl disulfide all dissolve readily in liquid SO_2. So far as I am aware this method of refining has not been applied to gasolines, nor is it apparent why it would be advantageous. It is not desired to remove unsaturated and aromatic hydrocarbons. Also the necessary apparatus is more complicated than that

[35] "Handbook of the Petroleum Industry"—Edited by Day. Vol. II, 369-70. See also U. S. Patent 1,187,797, issued to D. M. Allan, Jr., June 20, 1916.
[36] U. S. Patent 911,553, Feb. 2, 1909.
[37] U. S. Patents No. 1,152,478, Sept. 7, 1915. No. 1,164,162, Dec. 14, 1915.
[38] *J. Inst. Pet. Tech.*, 3 (1917), 247-8.

used in treating with sulfuric acid. The writings [39] of several other investigators may be referred to for fuller information.

Use of Silica-Gel.

Silica-Gel, made by the coagulation of a colloidal solution of silicic acid, is a material possessed of remarkable adsorptive properties. The use of this product in refining distillates offers most interesting possibilities. It is claimed by its makers [40] that it is capable of producing a refined product that is water-white, and that has a sweeter odor and lower sulfur content than ordinary gasoline. It is claimed that the treatment with Silica-Gel is so effective that the product will remain water-white on exposure to sunlight for an indefinite period. It is further claimed that cracked gasolines can be refined with Silica-Gel without large volumetric loss. The process of refining with Silica-Gel consists in agitating the distillate in successive stages with the powdered reagent, followed by decantation of the refined product. The spent Gel is treated with water to displace the adhering gasoline, and is re-activated by heating. I am of the opinion that the use of Silica-Gel and other adsorbents possesses interesting possibilities.

Use of Aluminum Chloride.

Gasolines of excellent quality can be prepared by the use of aluminum chloride in refining. The anhydrous chloride, however, combines so readily with the olefins that it is difficult to see how it could be used with advantage in refining distillates containing large amounts of these substances. So far as I can see it is not possessed of a sufficient advantage over sulfuric acid to warrant its use as a refining reagent, however useful it may be in the production of high-grade gasoline from heavy oils.

Use of Hypochlorous Acid or Hypochlorites.

The use of hypochlorous acid in refining gasoline and removing sulfur has been discussed above. The use of hypochlorites in sweetening natural gasoline is described in Chapter XI.

Use of Saponaceous Material.

C. K. Francis [41] and D. C. Morgan have patented a process claimed to produce gasoline of first quality from olefinic distillates. The acid and alkali treated distillate are thoroughly mixed with a reagent that may consist of lard 2 parts, NaOH 0.3 part, and soda-ash 3 parts, and then distilled. About one pound of this reagent should be used for each barrel of distillate.

[39] Ubbelohde, *Z. f. Angew. Chem.*, 26, 177-81. Anon., *Chem. Tech. Ztg.*, 30, 71. Gad, E., *Pet.*, 4 (1908), 324. Rittman & Moore, *Met. Chem. Eng.*, 13 (1915), 713.

[40] The Silica-Gel patents are controlled by the Davison Chemical Co.

[41] U. S. Patent 1,313,629, Aug. 19, 1919.

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Chapter XI.

Natural-Gas Gasoline.

The recovery of gasoline from natural gas is in every sense an industry based on true conservation. Starting in 1903-1904 with the efforts of A. Fasenmeyer near Titusville, Pa., of Tompsett Bros., at Tidioute, Pa., and of Sutton Bros., at Sisterville, W. Va., operations expanded to such an extent within less than two decades as to comprise an industry the value of whose products is over $75,000,000 annually.

According to F. P. Peterson,[1] who has been identified with the business since its inception, real commercial development started near Kinzua, Pa., where a small plant was built by John L. Gray in the years 1907-1910. Other commercial developments that followed closely were those at Sisterville, W. Va., and at Bolivar, N. Y.

The first gases to be handled were those from the casingheads of the oil wells, that is, the gas flowing from between the tubing and the casing. The volume of this gas from a single well may be as low as two or three hundred cubic feet, or as high as forty to fifty thousand cubic feet per day. Were it not for the recovery of casing-head gasoline, a large part of the gas would be wasted, since it would be unprofitable to collect it for sale as gas alone. But with the added incentive of profits from the sale of gasoline, gathering systems have been constructed, and gas and gasoline have been conserved. A single plant in Western Pennsylvania collects gas from 1500 oil-wells, the average gas yield per well being only 350 cu. ft. per day. Fifty-one miles of pipe, ranging in size from 2 to 8 feet, is required. Were it not for the gasoline recovered the collection of this gas would not be economically possible.

Not only should the natural gas industry be commended for conserving a valuable natural resource, but also for making available a product of the greatest value. Only a few years ago casinghead-gasoline, as it was then called, acquired a bad reputation through the marketing of casinghead-kerosene blended fuels. Inexperience, ignorance, and in some cases lack of scruples were responsible for the sale of these highly unsatisfactory motor-fuels. Now the lesson has been learned, and gasoline from natural-gas is highly valued for blending with naphthas, and with cracked or straight-run gasolines that contain too little of the more volatil components. There is no excuse for prejudice against the proper use of natural-gas gasoline. The hydrocarbons contained in this product are the most valuable and useful that

[1] *Trans. Am. Inst. Min. Eng.*, 1918, 2076.

it is possible to obtain. The present tendency is toward the addition of smaller quantities—10 to 15 per cent—to gasolines, and somewhat larger quantities to naphthas, in order to lower the initial boiling point and increase the proportion boiling under 221° F., rather than to make motor fuels containing 40 to 60 per cent of natural-gas gasoline and 60 to 40 per cent of some relatively heavy distillate.

The methods now in use for the production of gasoline from natural gas are, (1) the compression method, (2) the absorption method, (3) the adsorption method. The compression method was the first to be used, the absorption method was of little importance prior to 1915, and the processes involving adsorption of the gasoline by charcoal or silica-gel have been used for two or three years only. Statistical tables showing the growth of the industry as a whole, its extent in the several states, and the relative importance of the processes are given at the end of the chapter.

In the years 1916 and 1917 the expansion of the industry was very rapid. Production in 1916 was almost double that of 1915, and in 1917 was more than double that of 1916. Since 1918 growth has been steady, but at a rate more nearly the same as that of the petroleum industry as a whole. In 1911 the volume of gas treated was only 0.5 per cent of the total natural gas produced, in 1916 it was 27.7 per cent, and in 1919 39 per cent.

The natural-gas gasoline industry was prosperous until the end of the year 1920. But the rapid expansion of the industry, carelessness and lack of technical knowledge on the part of many operators, and an insistant and growing demand led to the marketing of highly volatile products that were dangerous to ship and difficult to handle without excessive loss. Bad conditions led to worse and contributed to the chaos of late 1920 and early 1921 that was precipitated by the credit-deflation of this period. The industry as a whole had its first taste of business depression. Natural-gas gasoline became a drug on the market, tanks were full by May of 1921, and prices dropped to 8-9 cents per gallon and even to 5-6 cents at some Texas points. The appearance of the highly volatile products led the Bureau of Explosives to draw rules for its shipment that caused many producers to operate at a loss.

The necessity for better organization and for standardization was most apparent. The outcome was the organization of the Association of Natural Gasoline Manufacturers. Specifications[2] were drawn by this Association that have done much to establish uniformity of product, and to stabilize the industry. The value of natural-gas gasoline to the refiner, also, is too great long to permit a poor market for the carefully made product. Bad as the reputation of casinghead-kerosene blends may have been, the intelligent refiner is quick to recognize the value of natural-gas gasoline when properly used. The clouds of early 1921 faded away, and in the latter part of that year good markets again prevailed.

[2] See section on specifications in this chapter.

Consideration of the history of the industry, and of the intrinsic value of the product, lead me to the conclusion that the demand for natural-gas gasoline will soon exceed the supply. The period of rapid expansion of the industry is over, for the simple reason that most of the gases that can be handled with profit are now being treated. The volume of natural-gas gasoline now made is 8 per cent of the total gasoline production in this country. At least another 4 per cent of the present gasoline supply should in all fairness be credited to the natural-gasoline industry on account of the naphthas and other distillates that are rendered available as satisfactory fuels through blending with natural-gasoline. In all, therefore, the industry is responsible for approximately one-eighth of our present gasoline production. It is clear that the natural-gasoline industry cannot furnish the additional motor-fuel that will be needed ere long, for, from this time on, the growth of the industry will be slower and commensurate with that of the petroleum industry as a whole. The trend will be toward consolidation, and standardization of product and technical methods. The fireworks is over. It is now a case of "sawing wood."

The Composition of Natural Gases.

Natural gases are composed of hydrocarbons and small quantities of carbon dioxide, nitrogen, and sometimes hydrogen sulfide. Olefin hydrocarbons, hydrogen, and carbon monoxide have never been found in natural gases examined by the U. S. Bureau of Mines.[3] The oxygen that is frequently reported in analyses probably becomes mixed with the gas as a result of faulty sampling or leaks in pipes or apparatus. Helium is found in the gases from a few districts, notably in Texas.[4] The hydrocarbons methane, propane, butane, pentane, hexane, and heptane are present in proportions that depend on whether the gas is produced from a gas-sand or an oil-sand, on the character of the petroleum, in the event of production from an oil-sand, and on the pressure. Methane, ethane, and propane are gases at ordinary temperatures and pressures. The boiling point of methane is —164° C., of ethane —89.3° C., and of propane —44.1° C. N-Butane boils at 1.0° C. at 760 mm. pressure. The pentanes, hexanes, and heptanes are liquids at ordinary temperatures and pressures. In a general way the vapor pressure of the hydrocarbons at any given temperature decreases with increase in molecular weight. This can be seen from an inspection of Table LXI that gives the vapor pressures of several of the lower molecular weight paraffin hydrocarbons. For instance at 0° C. or 32° F. the vapor pressures are approximately: n-propane 3775 mm., n-butane 780 mm., n-pentane 183 mm., n-hexane 45 mm., and n-heptane 12 mm.

Gases that issue from the well under several hundred pounds pressure are composed largely of methane and ethane, while those from

[3] U. S. Bur. of Min., Tech. Paper 10, p. 8.

[4] Rogers, G. S., "Helium-bearing Natural Gas." U. S. Geol. Sur., Prof. Paper 121 (1921).

TABLE LXI

VAPOR PRESSURE OF SEVERAL PARAFFIN HYDROCARBONS

MILLIMETERS OF MERCURY *

Propane [a]		N-Butane [b]		Iso-Butane [b]		N-Pentane [c]		N-Hexane [c]		N-Heptane [c]	
t.°C.	mm.	t.°C.	mm.	t.°C.	mm.	t.°C.	mm.	t.°C.	mm.	t.°C.	mm.
—124.2	3	—113.1	0.3	—114.8	1.0						
—100.5	30	— 99.9	1.0	— 98.4	7.0						
— 71.1	200	— 75.6	15.0	— 72.7	50.0						
— 53.2	500	— 47.5	100.0	— 41.1	300.0						
— 44.1	760	— 34.6	200.0	— 34.1	400.0						
— 19.0	2052	— 18.1	400.0	— 19.1	650.0						
+ 1.0	3876	— 0.3	760.0	— 13.4	760.0	0.0	183.3	0.0	45.5	0.0	11.5
12.5	5396	......	......	......	......	10.0	281.8	10.0	75.0	10.0	20.5
22.0	6840	30.0	2550.0	30.0	3400.0	20.0	420.2	20.0	120.2	20.0	35.5
53.0	12920	50.0	4300.0	50.0	5600.0	37.0	760.0	30.0	185.4	30.0	58.4
85.0	26600	90.0	10700.0	90.0	13000.0			69.0	760.0		
102.0	36860	100.0	12500.0	100.0	15400.0					98.4	760.0

* It should be noted that the data for the several hydrocarbons, although given on the same line, are not necessarily for the same temperature.

[a] First five figures from Burrell and Robertson, *J. Am. Chem. Soc.*, 37 (1915), 2188-93. Last five from Meyer, L., *Ber.*, 27 (1894), 2768. Burrell and Robertson's work is more accurate than Meyer's.

[b] Burrell and Robertson, *J. Am. Chem. Soc.*, 37 (1915), 2188-93. Seibert and Burrell, *J. Am. Chem. Soc.*, 37 (1915), 2691.

[c] Burrell, Seibert and Oberfell, *Bull. 88*, U. S. Bur. Min., 28.

casingheads of wells under a vacuum contain large percentages of propane, butane, pentane, hexane, and some heptane and octane. The principles that are discussed below in connection with the compression process furnish a ready explanation of these facts.

Natural gases are classed as "dry" or "wet" depending on the content of pentane, hexane, and heptane. The wet gases are those that

TABLE LXII

TYPICAL ANALYSES OF WET AND DRY NATURAL GASES [a]

	Wet Gas	Dry Gas
Methane	36.8	84.7
Ethane	32.8	9.4
Propane	21.1	3.0
Butane	5.8 }	1.3
Pentane and Hexane	3.5 }	
Nitrogen	0.0	1.6
	100.0	100.0

[a] These analyses were made by the method of fractional distillation in a vacuum. They are reported by Burrell and Oberfell, U. S. Bur. Min., 8-9, Tech. Paper 109.

TABLE LXIII

Properties of Natural Gas Hydrocarbons

	A	B	C	D	E	F	G	H	I	J	K	L
						Specific Gravity						
Name	Formula	Melting Point °C.	Melting Point °F.	Boiling Point °C.	Boiling Point °F.	Gas Air = 1	Liquid Water = 1	Gravity Baumé Scale	Vapor Pressure 60° F. In. Hg.	Cu. Ft. Vapor per Gal.	Gal. per M Cu. Ft. Sat. Vapor	B. t. u. per Cu. Ft.
Methane ...	CH_4	—184.0	—299.0	—160.0	—256.0	0.554	.....	.....	.....	....	.....	1008.5
Ethane	C_2H_6	—172.1	—277.8	—84.1	—119.4	1.038	.....	.....	.....	....	.....	1763.2
Propane ...	C_3H_8	—187.8	—206.2	—44.1	—47.4	1.523	.....	.....	.....	....	.....	2518
Butane	C_4H_{10}	—135.0	—211.0	+0.3	+32.5	2.007	0.600	103.3	63.00	....	.....	3273
Pentane ...	C_5H_{12}	—130.8	—203.4	36.4	97.7	2.491	0.626	93.6	13.99	27.3	17.1	4027
Hexane	C_6H_{14}	—94.0	—137.2	69.0	156.2	2.975	0.663	81.2	3.82	24.2	5.26	4782
Heptane ...	C_7H_{16}	—97.1	—142.8	98.4	209.2	3.459	0.688	73.5	1.02	21.6	1.57	5537
Octane	C_8H_{18}	—56.6	—69.9	125.5	257.9	3.944	0.707	68.0	0.31	19.5	0.53	6291
Nonane	C_9H_{20}	—51.0	—59.8	150.5	302.9	4.428	0.722	63.9	0.16	17.7	0.30	7046
Decane	$C_{10}H_{22}$	—32.0	—25.6	173.0	343.4	4.912	0.734	60.7	0.08	16.2	0.16	7801
Undecane ..	$C_{11}H_{24}$	—25.6	—14.1	194.5	382.1	5.396	0.743	58.4	0.03	15.0	0.07	8555

Columns B and D—The values for the melting and boiling points that are given in Columns B and D were taken from the 1918 edition of Van Nostrand's "Chemical Annual." The boiling point of ethane was determined at a pressure 749 mm., and that of nonane at 759 mm.; otherwise the figures are for 760 mm.

Column F—Theoretical specific gravities are given in Column F. They were computed from the formula sp. gr. $= 0.4842\,n + 0.07$, in which n represents the number of carbon atoms in the hydrocarbon molecule (see Anderson, *J. Ind. Eng. Chem.*, 11 (1919), 299).

Column G—The figures in Bernthsen's "Organic Chemistry," 1912 Edition, page 30, form the basis of Column G, corrections having been applied to obtain the ratio of the weights of hydrocarbon and water at 60° F. No correction has been made to the value for butane which was determined at its boiling point.

Column H—The Baumé scale figures in Column H were computed from the values in Column G by the formula: Degrees, Baumé $= \dfrac{140}{\text{Sp. Gr. } 60°/60° \text{ F.} - 130}$, in accordance with the procedure adopted by the Bureau of Standards. (See *Circular* 57.)

Column I—The vapor pressures at 60° F. given in Column I were taken from curves prepared from tables in Landolt-Börnstein, "Physikalisch-chemische Tabellen," with the exception of the values of nonane and undecane, which were gotten from the others by interpolation.

Column J—The volume of dry vapor at 60° F. and 30 in. mercury corresponding to one gallon of the important gasoline hydrocarbons, as given in Column J, was computed from the formula:

$$\frac{\text{Wt. gallon water at 60° F.} \times \text{Sp. Gr. Hydrocarbon (Water} = 1)}{\text{Wt. cu. ft. dry air at 60° F. 30 in. Mer.} \times \text{Sp. Gr. Hydrocarbon (Air} = 1)} = \frac{8.328}{0.07650} \times \frac{\text{Sp. Gr. Hydrocarbon (Water} = 1)}{\text{Sp. Gr. Hydrocarbon (Air} = 1)},$$

Column K—Column K shows the theoretical yield of the various gasoline hydrocarbons expressed in gal. per M cu. ft. of gas at 60° F. and 30 in. mercury. The yields were computed by the formula:

$$\text{Gal. per M cu. ft.} = \frac{\text{Vapor Pressure}}{30} \times \frac{1000}{\text{Cu. ft. per gal.}} = \frac{\text{Vapor Pressure} \times 33.3}{\text{Cu. ft. per gal.}}.$$

Column L—The heating value of dry gas at 60° F., 30 in. mercury, as given in Column L, was computed from the formula: B. t. u. per cu. ft. $= 253.8 + 754.7\,n$, in which n represents the number of carbon atoms in the hydrocarbon molecule.

contain a sufficient quantity of these hydrocarbons to yield over one gallon of liquid condensate per 1000 cu. ft. Dry gases are those that contain a lesser proportion of these condensible hydrocarbons.

Casinghead gases and natural gases that are produced under moderate pressures, and that have been in contact with petroleum containing a large proportion of the volatil hydrocarbons, are wet gases. They yield one to six gallons of condensate per 1000 cu. ft. of gas. Dry gases are those that issue from the ground under pressure that has been sufficient to liquefy the larger part of the hydrocarbons of molecular weight higher than that of propane. In some districts gases are found that are composed almost entirely of methane, or of methane and small amounts of ethane. Possibly these might be designated as "extra dry." Obviously no gasoline can be made from them.

The composition of the natural gases of this country have been the subject of a number of government bulletins [6] to which the reader is referred.

For convenient reference Table LXIII is given showing the properties of the substances of which natural gases are composed. The table was compiled by Dr. R. P. Anderson.[7]

The Compression Process for Making Natural-Gas Gasoline.

Three quarters of the natural-gas gasoline produced today is made by the compression process. This method consists in treating the gas by a combination of compression and cooling, as a result of which a liquid mixture of hydrocarbons is formed.

The early history of the manufacture of natural-gas gasoline has been briefly reviewed. Fasenmeyer made 4000 barrels of 80 to 90° Bé. gasoline during the first year of his operations. The gas was pumped under pressure into water-cooled coils, and the condensate collected in wooden barrels.[8] William Richards of Mayburg and Warren, Pa., claims to have been the first to use high-pressure compressors. In his experiments in 1905 he used pressures of about 400 lbs. per sq. in., but later came to the conclusion that 250 lbs. was sufficient. As I have already stated, Peterson considers that active commercial development started with John L. Gray's plant built during the years 1907-1910 near Kinzua, Pa. The following referring to Gray's plant is quoted

[6] Allen and Burrell, "Liquefied Products from Natural Gas," U. S. Bur. Min., Tech. Paper 10, 1912. Burrell, "The Suitability of Gasoline for Making Gasoline," U. S. Bur. Min., Tech. Paper 57, 1913. Burrell and Oberfell, "The Composition of the Natural Gas Used in Twenty-five Cities," U. S. Bur. Min., Tech. Paper 109, 1913. Burrell and Robertson, "The Compressibility of Natural Gas and Its Constituents with Analyses of Natural Gas from Thirty-one Cities in the U. S.," U. S. Bur. Min., Tech. Paper 158, 1917. Clarke, F. W., "The Data of Geochemistry," U. S. Geol. Sur. (1920), *Bull. 695*. Phillips, F. C., "Composition of Natural Gases," *8th Int. Cong. App. Chem.*, 25 (Appendix), 719. Burrell and Seibert, "Composition of Natural Gases," *8th Int. Cong. App. Chem.*, 25 (Appendix), 637.

[7] *J. Ind. Eng. Chem.*, 12 (1920), 548.

[8] H. Botsford, *Pet. Mag.*, May, 1920, 29.

from an article[9] by Peterson, "In 1910 it was operating continuously and successfully, and in its operation were embodied every detail of development that has been worked out to this date, with the exception of increased pressure. The pressure maintained in that little operation was from 90 to 110 lbs. per sq. in., gage, using a single-stage, belt-driven compressor. The details of equipment, including automatic liquid traps, were similar to those of modern installations. Refrigeration of the gas under pressure was effected by taking advantage of the latent heat of vaporization of the light cymogene or rhigolene vapors as the liquid condensate was relieved from under operating pressure of the gas. This installation even went so far as to saturate the incoming gas by bubbling it up through the crude oil produced from the lease, and, at the same time, raising the temperature of the crude to a degree that encouraged the throwing out of a light gasoline fraction from the oil. Attached to the crank shaft of the compressor by means of a small eccentric, was a tiny pump cylinder of 7/8-in. bore by 3/4-in. stroke, as I recall it. This little pump forced a naphtha stream into the discharge pipe line directly after the connection on the compressor cylinder. The naphtha was atomized and probably partially vaporized and carried along with the stream of gas under pressure, combining the functions of operation into a fairly well worked out absorption plant. The blended product from this plant was as good as that from a most modern equipment operating on the larger scales of the present day. It is only within the last two years that this method of blending has been more or less generally adopted as the best practice in the Oklahoma fields where a high degree of efficiency has been reached. Further history of the industry has little to add in the way of details of equipment and method of operation."

Thus speaks the man of whom John D. Northrop says in "Natural-Gas Gasoline in 1917" when referring to the growth of the natural gasoline industry, "Little headway was made until 1909 and 1910, when the researches of Peterson and his associates on the engineering staff of the Bessemer Gas Engine Company of Grove City, Pa., transformed the industry from an experimental basis to a commercial one."

The gases used in making natural-gas gasoline by the compression process are casinghead-gases, or other "wet" gases. These may be collected from the casingheads of the wells as is done in Pennsylvania where the gas is drawn from the well under a vacuum of 20 to 26 in. of mercury, from flow-lines or flow-tanks as in some instances in Oklahoma, or from traps as in California. Traps are ordinarily designed and used for the purpose of scrubbing the gases with petroleum in order to absorb part of the pentane, hexane, and heptane, and thus increase the gasoline content and value of the oil. The operation of traps is now, in some instances, exactly the opposite. The trap is held under a vacuum while the oil and gas are brought into contact within. The more volatil portion of the oil vaporizes and is recovered, along with the heavier hydrocarbons of the gas, when the gas is treated by com-

[9] *Trans. Am. Inst. Min. Eng.*, 1918, 2076-7.

pression and refrigeration. This procedure is most profitable when the crude is necessarily stored for some time before being refined.

Gas from whatever source is led through pipes, usually 2-in., to a gas main through which it is conducted to the compression plant. If the gathering system is not too extensive the vacuum produced by the low-pressure cylinder of the compressor will be sufficient to move the gas through the line. If the gathering system is complicated and extensive, several sub-stations with gas-pumps are required to move the gas and to hold the wells under the desired vacuum. The design of the gathering system as to location of vacuum and booster stations, and as to pipe sizes and location of drips, should be carefully studied. Helpful information on the flow of gases in pipes will be found in Chapter IV.

In locating the plant, important factors are transportation facilities, water-supply, and the length of gathering lines and dry-gas lines. In the Western districts a suitable supply of water may be difficult to find.

Theoretical Basis of the Compression Process.

The compression process for the recovery of gasoline from natural gas is based on a few simple physical principles. Consider that several hundred cubic centimeters of liquid n-hexane are placed in a vertical cylinder, closed at one end, and fitted at the other with a piston that is free to move. Assume that the mass of the piston is zero, that no force is required to move it along the cylinder, that weights can be placed on the piston as desired, that the entire apparatus is in a vacuum, and that the temperature of the system can be changed at will. Observation of the system starts when the piston is in contact with the liquid at a temperature of 0° C. The weights on the piston are then removed. At once the piston moves up the cylinder. Vapor is formed continuously as a result of the escape of the more rapidly moving molecules of hexane from the vicinity of the surface of the liquid. If weights are now placed on the piston until the force is equal to that exerted by a column of mercury 45.5 mm. high the piston comes to rest. The force on the under side of the piston is that resulting from the impact of the hexane molecules on the surface of the piston. This is exactly balanced by the weights. The system is in a condition of equilibrium. Molecules leave and enter the surface of the liquid in exactly the same number. The force on the piston, expressed usually in millimeters of mercury, is known as the vapor-pressure of the liquid at the temperature of the system, and is a specific physical property of the substance n-hexane.

If now another weight is added to those already in place, the piston moves downward and the pressure within the cylinder increases momentarily since the molecules in the vapor are packed into a smaller volume. The molecular concentration, that is, the number of molecules per unit volume, is greater. This results in increasing the number of molecules that impinge on each unit area of the liquid surface. Since more molecules enter the liquid than leave it, the number in the vapor

space becomes less. Both the absolute number of molecules in the vapor and the molecular concentration of the vapor decrease, the piston drops, and the process ends only when all the molecules that formed the vapor have entered the liquid.

If now the weights are removed from the piston, and the temperature of the system raised to 10° C., molecules again leave the liquid and form a vapor phase. The vapor-pressure can again be balanced by placing weights on the piston, but more weights are required than before. In fact, the weights that will just balance the vapor-pressure are found to be equivalent to a mercury column 75.0 mm. in height. The vapor-pressure of the liquid is greater at the higher temperature. But again the vapor can be completely condensed if the weight on the piston is slightly increased above that that balances the vapor-pressure of the liquid.

If natural gas were composed entirely of hexane vapor, all that would be required to obtain liquid hexane at a temperature of 20° C. would be to maintain a pressure slightly greater than 120.2 mm. of mercury on the gas or vapor. But, as we have seen, natural gas is composed of a number of hydrocarbons from methane to octane. For simplicity assume that a gas from which it is desired to produce liquid hexane contains 90 per cent methane and 10 per cent hexane by volume. How can the hexane be obtained in liquid form if the temperature is 20° C. and the total pressure 760 mm. of mercury? Dalton's law of partial pressures states that the total pressure of a gaseous mixture is equal to the sum of the partial pressures of the component gases. If the total pressure is doubled, by compressing the gas into one-half its original volume, the partial pressure of each component is also doubled, provided the gases are "perfect" gases and follow Boyle's law. This is not strictly true of the hydrocarbons, but for the moment hexane vapor will be considered a perfect gas. Since the gaseous mixture contains 10 per cent by volume of hexane, one molecule in every ten is a hexane molecule, and the partial pressure of the hexane is 76 mm. of mercury. If the gaseous mixture is placed in the cylinder with the frictionless piston weighted to produce a total pressure of 760 mm., and then more weights are added, the volume becomes less, and the total pressure greater. The partial pressure of the hexane increases with no apparent effect until, at 120.2 mm. partial pressure of hexane liquid hexane starts to form. At this time the total pressure is $760 \text{ mm.} \times \frac{120.2}{76} = 1202 \text{ mm.}$ A very minute quantity of the liquid will form, however, since the formation of the liquid decreases the number of molecules in the vapor, that is, decreases the partial pressure. Hence the total pressure must be further increased if more liquid hexane is to be formed. When the total pressure reaches 2404 mm. one-half of the hexane will be liquefied, and one-half will still be gaseous. Nine-tenths of the hexane will be liquid when the total pressure is 12,020 mm. of mercury or 232.4 lbs. per sq. in. absolute, and 99 per cent when the pressure is 120,200 mm. or 2324 lbs. per sq. in.

Thus, while it is easy to obtain part of the hexane in liquid form, excessive pressures must be used to liquefy 95 per cent or more.

The gaseous mixture considered in this example is comparable to a rich casinghead gas. From each 1000 cu. ft., over 3 gallons of liquid hexane would be produced. In order to avoid the use of excessive pressures, advantage is taken of physical relationships that have already been briefly mentioned. The vapor-pressure of a liquid substance increases with temperature. In order to form the liquid hydrocarbons from natural gases it is only necessary to compress the gas until the partial pressure of the components exceeds the respective vapor-pressures. This statement is not entirely rigorous, as will soon be shown,

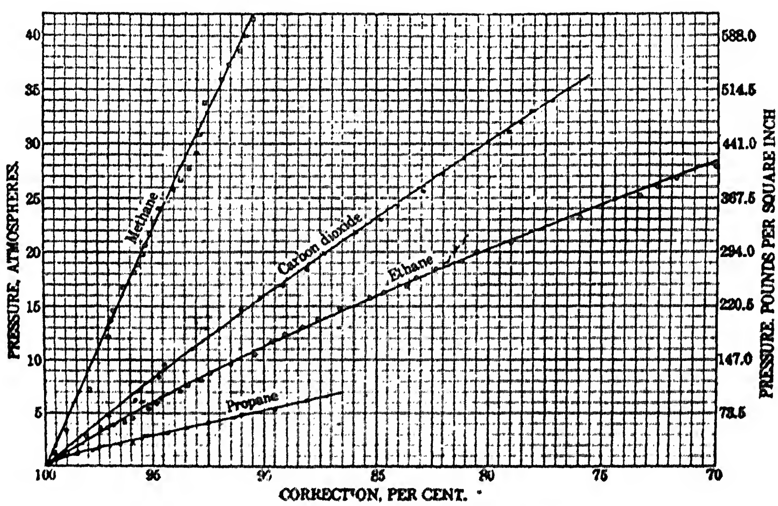


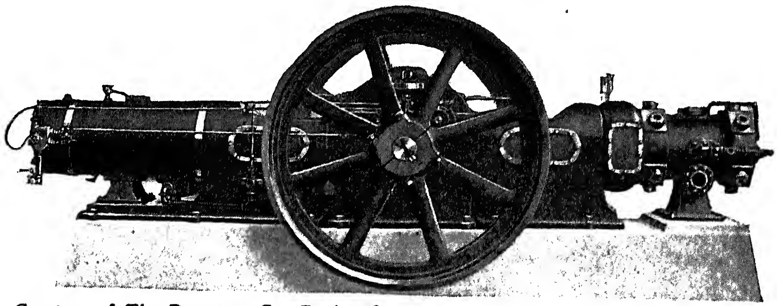
FIG. 125.—Compressibility of Gases.

but may be kept in mind for the moment. In view of these facts the obvious procedure is to cool the gas as well as to compress it. At the lower temperatures vapor pressures are less, and consequently partial pressures need not be so great in order to exceed the vapor pressures. Hence the commercial use of both compression and cooling in making natural-gas gasoline.

Now that the principles involved have been reviewed and illustrated by simple examples, it is time to consider to what extent and how rigorously they can be applied in practice. Natural gases are mixtures of several hydrocarbons, and when treated by compression and cooling form liquids that contain several hydrocarbons. The composition of the liquid hydrocarbon mixture or casinghead gasoline depends on that of the gas from which it is made. In Chapter IV I have already discussed the subject of the vapor pressure of mixtures of two or more liquids. Just as the vapor that forms in the distillation of binary or

more complex mixtures contains the several components, so liquids formed from vapor mixtures are mixtures whose composition is a function of that of the vapor. One is not so much concerned with the partial pressures of the individual components as with the vapor-pressures of various hydrocarbon mixtures. The subject becomes entirely too complicated in actual practice to allow of mathematical calculation. In making gasoline, pure heptane does not first condense, followed by hexane and pentane, but that liquid mixture is formed whose vapor-pressure is first exceeded.

A further complication is introduced through the fact that the vapors of heptane, hexane, pentane, butane, and propane do not behave as perfect gases, that is, they do not follow the laws commonly known as those of Boyle and Charles. The compressibility of methane, ethane,



Courtesy of The Bessemer Gas Engine Company.

FIG. 126.—Bessemer Type 8, Direct Gas-Engine Driven Compressor.

and propane has been investigated by Burrell and Robertson,[10] and Burrell and Jones,[11] and is shown in Figure 125. References to other work in this subject will be found in their publications. The compressibility of the hydrocarbons of higher molecular weight is greater, but has never been carefully investigated. Hence it is quite beyond possibility to calculate just what will happen to a given mixture of hydrocarbon gases when it is cooled and compressed to a given temperature and pressure. Our physical laws are a most valuable guide in a qualitative way, but cannot be quantitatively applied in the present state of our knowledge.

Compression Plant Practice.

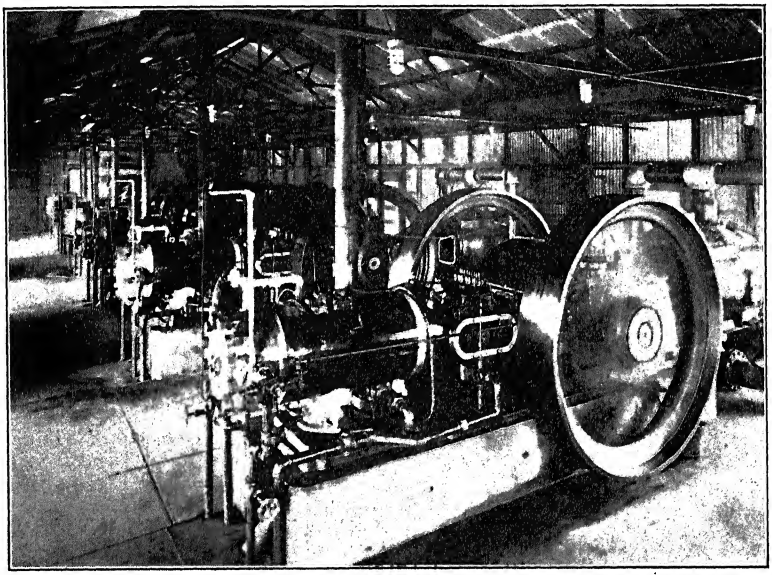
The gas entering a compression plant is passed through a receiving tank or scale tank that is provided with baffles, and which serves to clean the gas from dirt and scale. It should be precooled to 60 to 70° F.

[10] U. S. Bur. Min., Tech. Paper 131, "The Compressibility of Natural Gas at High Pressures." (1916.) U. S. Bur. Min., Tech. Paper 158, "Compressibility of Natural Gas, etc." (1917.)

[11] U. S. Bur. Min., Ser. 2276, "Pressure-Volume Deviation of Methane, Ethane, Propane, and Carbon Dioxide at Elevated Pressures." (1921.)

before passing to the first stage of the compressor. The volume of the gas is thus reduced, and the compressor will handle a larger weight of gas in unit time. A trap or liquid separator should be placed between the precooling coils and the first stage of the compressor in order to avoid entry of liquid into the cylinder.

The compressors commonly used in the manufacture of gasoline are specially designed two-stage machines. See Figures 126 and 127. Manufacturers' catalogs should be consulted for description of this equipment. The gas enters the low-pressure cylinder at 0 to 3 lbs. abso-

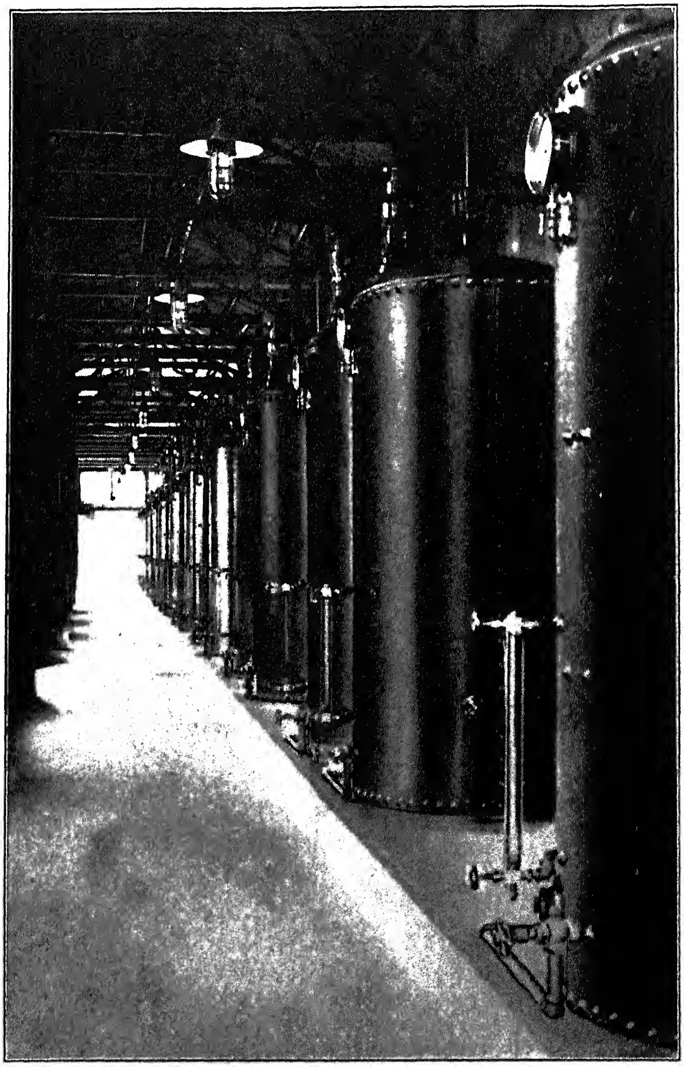


Courtesy of The Bessemer Gas Engine Company.

Fig. 127.—Natural Gasoline Compression Plant of Wolverine Oil Company at Bartlesville, Showing Six 80-H.P. Type 8 Bessemer Compressors.

lute, and is compressed to 40 to 60 lbs. gage or 55 to 75 lbs. absolute. The temperature of the gas from the low-pressure cylinder is 200 to 250° F. The hot gas is passed through a lubricating-oil separator, and then to cooling coils that are an elaboration of the intercooler of the ordinary air compressor and in which the gas is cooled to 60 to 70° F. The subject of cooling coils is discussed in Chapter VII, and the theory of heat transfer in Chapter V. A common type of coil consists of 2-in. pipe connected by return bends or special fittings. Water is sprayed or trickled over the coil, or it is immersed in a tank of water. 0.5 to 0.7 sq. ft. of external surface per 1000 cu. ft. of gas treated, or 2.5 to 4.0 sq. ft. per h. p. used in compression is common practice in design. Where water is none too plentiful air-cooling coils are frequently used in conjunction with the water-cooled coils.

The flow of gas and condensate should be in the same direction through the coil. Otherwise the liquid film within the pipe will be too thick, and the transfer of heat needlessly slow. The current idea that



Courtesy of The Bessemer Gas Engine Company.

FIG. 128.—Accumulator-Tank House, Pure Oil Company, Dawes, W. Va.

it is best practice to limit the time of contact between gas and condensate as far as possible is erroneous. The cooling-coil functions in essentially the same manner as a constant temperature reflux or partial

condenser.[12] The tendency is to bring a complex two-phase system into equilibrium at some temperature. The longer and more complete the contacting of liquid and gas phases the more nearly will this be accomplished. In practice, of course, the coil does not function as a single temperature apparatus, but over a limited temperature range. This, however, does not invalidate the above reasoning. If the flow of gas is upwards, and the flow of liquid downwards, the liquid formed in the lower part of the coil will be composed of the relatively less volatil hydrocarbon components, and that in the upper lengths of the coil of somewhat more volatil components. As the condensate from the upper portion of the coil runs downward in contact with the gas, part of the more volatil substances will vaporize and be replaced by less volatil substances. The actual volume of condensate will not be changed as a result of this process, for the latent heats of the several hydrocarbons are not greatly different and the capacity of the coil for forming liquid is in the last analysis dependent on its efficiency as a means of transferring heat. It is true that downward flow through the coil produces more condensate than upward flow; but this is because of the obviously better heat transfer conditions when the coil is operated in this manner.

The gas and condensate from the cooling-coil is piped to an accumulator tank in which gas and liquid separate. These are pressure tanks, usually three to four feet in diameter and six to ten feet high. See Fig. 128. The gas inlet pipe enters near the top of the tank, turns downward and is discharged against a baffle plate so placed as to scrub out the liquid droplets and thus avoid their entrainment in the exiting gas. Accumulator tanks may be provided for each coil, or several coils may discharge into a single tank. Each tank is provided with pressure gage and gage glass.

The condensate in the accumulator tanks is removed by means of automatic traps that discharge to the "make tanks" or temporary storage tanks. The use of automatic traps avoids the results of possible negligence in the older method of "blowing" the accumulator tanks. Traps should be in duplicate so that if one fails to function properly no interruption of operations is entailed. The proportion of the condensate collecting in the low-pressure accumulator tanks will vary from a few per cent up to 40 per cent of the entire unblended product, depending on the composition of the gas and method of operation.

The gas from the low-pressure accumulator tanks, at a temperature of 60 to 70° F. is piped to the high-pressure cylinder of the compressor. Here it is compressed to about 250 lbs. per sq. in. gage or 265 lbs. absolute pressure. As a result of the work done on the gas the temperature again rises to 200 to 250° F. The gas entering the high-pressure cylinder should not contain droplets of condensate, for these will dissolve the lubricating oil in the cylinder and thus cause unnecessary wear. This difficulty may be overcome by placing a small scrubber, containing perforated concentric cylindrical baffles, in the gas-line, so that the droplets will be precipitated by impingement.

[12] See Chap. IV for a discussion of the theory of this apparatus.

The gas from the high pressure cylinder is passed through an oil-separator to remove lubricating oil that would discolor the product, and then to cooling coils. The coils used in practice are similar to those used to cool the gases from the low-pressure cylinder. 0.6 to 0.8 sq. ft. of external area per thousand cubic feet of gas, or 3.5 to 5.0 sq. ft. per horsepower used in compression, are common allowances in design. After passing through the cooling coils the gas and condensate are piped to the high-pressure accumulator tanks. The gas temperature should be not over 60 to 70° F. The liquid is trapped from the accumulator tanks as before. The condensate obtained at this point will be 60 per cent to nearly 100 per cent of the total unblended product.

In order to increase the yield of condensate various expedients have been used. The lower the temperature of the high-pressure gas the larger the yield of gasoline. In each instance there will be some limit beyond which it will not be profitable to go because the additional condensate will be largely butane and propane. However, it is probable that the possibility of obtaining additional recovery through cooling to low temperatures is under-rated and the above-mentioned limit placed too high. It is true that a "wild" product with an excessive vapor-pressure will be obtained, but this difficulty is easily overcome by proper "weathering." The erroneous impression lies in considering the process of liquid formation as consisting first in the formation of liquid heptane, then hexane, pentane, butane, and propane. The true manner of condensate formation has already been explained. The wild product formed when refrigeration of some sort is used contains worth-while proportions of pentane and hexane that need not be lost in the subsequent weathering.

In order to cool the gas leaving the high-pressure accumulator tank it may be allowed to do work in an engine. Some operators expand the gas through a valve, but the cooling effect is very small. By the use of an expansion-engine temperatures as low as —60° F. are obtained. The cold expanded gas is passed through an heat-exchanger counter-current to the compressed gas flowing to the expansion-engine. The yield of condensate may be increased 10 to 20 per cent by this means.

In 1915 a California plant built a refrigeration plant in which ammonia was expanded to cool brine in the usual way, and the cold brine then circulated to cool the compressed gas from high-pressure accumulator tanks. A plant of this type is described on page 66 of the U. S. Bureau of Mines *Bulletin No. 151*, and one using more extensive ammonia refrigeration on pages 63 to 66 of this bulletin. Circumstances in individual plants will determine whether the investment in equipment and additional costs of refrigeration are justified by the larger revenue.

A simple and satisfactory method of obtaining larger yields in a compression plant is to scrub the gas from the high-pressure accumulator tank with blending naphtha. The cost of suitable equipment is

small, and practically no attention is required to pump the naphtha through the absorber.

A flow-sheet of a compression plant is shown in Figure 129.

Character of Low-pressure and High-pressure Condensates.

The distillation range of the condensate from the low-pressure accumulator tank of a California plant is shown in Table LXIV. This

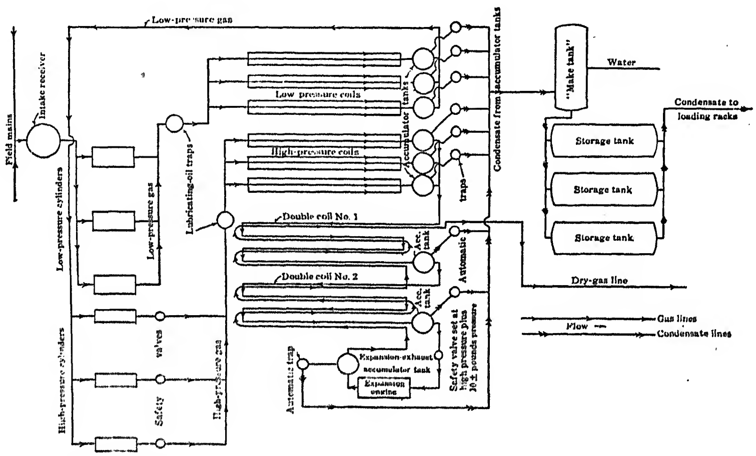


FIG. 129.—Flow-Sheet of Compression Plant, Using 2-Stage Compression and Single-Stage Expansion.

sample is representative of California practice. Eastern or Mid-Continent first-stage condensate of similar distillation range would have a Baumé gravity 5 to 7 degrees higher, thus indicating the presence of cyclic hydrocarbons in the California product.

TABLE LXIV[13]

DISTILLATION RANGE OF A 62° BÉ. FIRST-STAGE CALIFORNIA CONDENSATE

Per Cent Distilled	Temperature ° F.	Baumé Gravity of the Cut
Initial b. p.	106	....
10	174	76.8
20	192	71.8
30	206	66.5
40	218	63.1
50	228	60.8
60	241	58.4
70	254	56.5
80	272	54.6
90	312	51.4
End Point, 93%	352	

[13] U. S. Bur. Min., *Bull. 151*, 59.

Condensate from the high-pressure accumulator tanks is much more volatil than the low-pressure product. The Baumé gravity will be between 65° and 100°, probably averaging 85° in the East, 78° in Oklahoma, and 72° in California. The dissolved gas and more volatil portion of this condensate are evolved at ordinary temperature and pressure. Expansion-coil condensate is similar to that from the high-pressure accumulator tanks, though usually somewhat "wilder."

Effect of Air and Other Inert Gases on Gasoline Recovery.

In discussing the theory of the compression process I have shown that the presence of methane makes it much more difficult to condense hexane than if hexane vapor alone were treated. In the same manner other non-condensible gases such as the oxygen and nitrogen of the air, when mixed with the natural gas, render the recovery of the gasoline more expensive and less complete. The difficulties caused by air in natural-gas are summarized by Dr. O. J. Sieplein[14] as follows:

(1) Explosive nature of the material
 (a) causes excessive wear on the engine because of pre-ignition and rapid burning;
 (b) may result in wrecking of pipelines and other equipment.
(2) Inefficient production of gasoline
 (a) because of improper cooling after compression;
 (b) actual pressure in accumulators is lower;
 (c) gasoline vapor is carried out by air in the waste gas;
 (d) increases quantity of material handled;
 (e) effective pressure on the gasoline vapor is less.
(3) Excessive wear on the compressors
 (a) because of higher temperature of operation;
 (b) because the compressor cylinders are in contact with hot gas containing the oxygen of the air and are therefore corroded.

Air may be detected during the regular course of operation:

(1) By flames losing yellow color or blowing away from the burner.
(2) By increased temperature of the compression cylinders.

The presence of the inert hydrocarbon gases also is not always checked up closely enough by operators. Many cases are on record in which both the absolute yield of gasoline and the yield per unit volume of gas handled have been increased by cutting out the gas from various wells that were found upon test to be producing a lean gas. Analyses of the gases from various leases, and even from individual wells, should be made frequently enough to be certain that the gas taken therefrom is a source of profit rather than difficulty.

Water-vapor is an important component of the gas in some instances. A California plant produced 5 per cent as much liquid water as condensate. Natural gases contain some water vapor, and more is

[14] *Pet. Mag.*, July, 1921, 142.

introduced as a component of air that may leak into the gathering system. Carbon dioxide, too, is not uncommon as a component of natural gases. In California and in some districts of Oklahoma percentages as high as 10 are not infrequent, and as much as 30 per cent has been found.

Weathering Methods.

Natural-gas gasoline as made by the compression process contains too much butane, pentane, and dissolved propane and ethane to be suitable for storage or shipment, even after blending with less volatil naphtha. In order to conform to shipping regulations and to make a stable product the raw condensate must be "weathered."

A plant making 1,000 gallons of condensate per day should have three 10,000 gallon tanks for operating purposes. Naphtha for blending is stored in tank No. 1, raw condensate in tank No. 2 under about 15 pounds pressure, and tank No. 3 is used for weathering. When about 9,000 gallons of condensate is collected in tank No. 2 it is pumped to tank No. 3 where the temperature is raised by means of a coil heated with live steam, exhaust steam, or warm water from the engine jacket. A pressure of about 15 pounds should be held on tank No. 3, and the temperature slowly raised. The exact procedure necessary to produce a stable product must be determined in each plant. During the weathering process a vapor composed of large proportions of the gaseous and more volatil hydrocarbons, and smaller quantities of pentane, hexane, and heptane will be formed. The gas from the weathering tank should be piped to the intake of the low-pressure cylinder of the compressor in order that the valuable hydrocarbons may be condensed. In good practice the loss in volume of the liquid will be 5 to 20 per cent, and the decrease in gravity 2 to 3° Bé. Not infrequently weathering losses are as great as 40 to 50 per cent based on the volume of raw condensate.

Either raw-condensate or condensate blended with naphtha may be weathered. The use of blending, as discussed below, is so general that few plants weather raw condensate. Weathering is really nothing more or less than fractional distillation. The use of a tank or simple still is in truth the crudest way in which the desired result can be accomplished. A small continuous distillation plant, operated under pressure if necessary, would be far more effective than the methods now in general use. The liquid flowing from the bottom of the column would be the product for the market. The vapor from the reflux would be returned to the intake gas-line of the compression plant. A larger yield of a more uniform product would be made.[14a]

Blending.

A limited quantity of natural-gas gasoline is sold as 80 to 86° Bé. gas-machine gasoline, or as 74 to 80° Bé. export gasoline. The larger

[14a] Patent applications have been filed covering a process and apparatus for weathering condensate in an efficient manner.

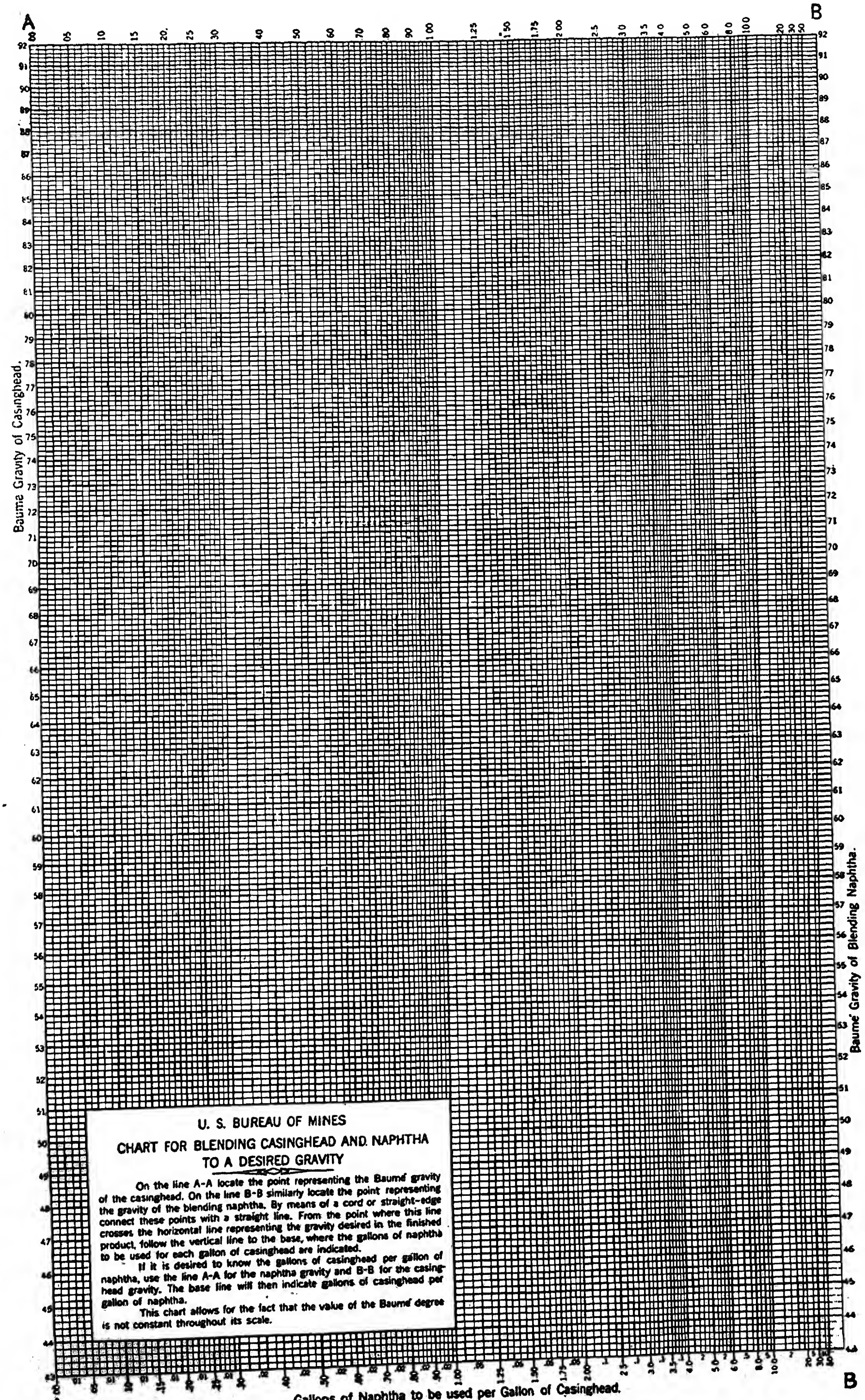


FIG. 130.—U. S. Bureau of Mines Chart for Blending Casinghead and Naphtha to a Desired Gravity.

part of the condensate is blended with light petroleum distillates of one kind and another. The blending is not always done at the compression plant. In some instances the raw-condensate is pumped under pressure through pipe-lines or shipped in other ways to petroleum refineries or to plants that make a business of blending and selling motor-fuels. Blending is used by compression plant operators because it is necessary in order that the product may be legitimately shipped under present regulations, and because it means money in their pockets. Weathering of unblended raw-condensate by the use of current methods, until the vapor-pressure is less than 10 pounds at 100° F., entails losses that may run as high as 75 per cent of the total liquid. If the condensate is first mixed with a suitable petroleum distillate the loss will be less than one-half these amounts.

Blending at the compression plant may be accomplished by injecting the naphtha into the high-pressure gas. This is known as "hot-blending" and is used when the natural-gas treated is rich in the more volatil hydrocarbons. Other plants blend in the accumulator tanks, or storage tanks. Blending is frequently done at the loading rack as this avoids transportation of the naphtha from the loading rack to the plant. Tank-cars are sometimes used as blending tanks. In blending in tanks the natural-gas condensate is pumped in at the bottom of the tank that already contains the naphtha. Stirring devices of a mechanical nature are not used. Frequently only a portion of the naphtha is added at the compression plant or loading rack. The partially blended product is further blended at the oil-refinery.

In making blending calculations it should be recalled that these must be based on specific gravities and not on Baumé degrees. Temperature corrections can be made by the U. S. Bureau of Standards tables for petroleum oils. Blending charts have been published by the U. S. Bureau of Mines, and by R. P. Anderson.[15] The chart of the Bureau of Mines is produced in Figure 130. For convenience the Bureau has expressed gravities as Baumé degrees.

The blending naphtha used in the Mid-Continent field is of 50 to 52° Bé. with an endpoint of about 450° F. or less. Eastern naphthas run from 52 to 54° Bé., and those of California 46 to 48° Bé.

The purpose of most blending today is not to produce a gasoline that is ready for the market, but as I have already stated, to make a product that refiners can add to their gasoline in amounts ranging from 10 to 15 per cent in order to increase the proportion of volatil hydrocarbons.

Miscellaneous Plant Details.

Lack of space forbids the discussion here of numerous important features of plant equipment and operation. The bulletins and books

[15] *J. Ind. Eng. Chem.*, 12 (1920), 1014.

referred to in the context and at the close of the chapter will be found to contain much valuable information, and reference should be made to them.

Natural-gas compression plants have been profitable when intelligently located and operated. In some districts plants handling only one hundred thousand cubic feet of rich gas have made money. In Western districts it is usually considered that a plant should produce at least 1000 gallons of marketable condensate per day if it is to be profitable. Depending on the size of the plant and on numerous other factors, the cost of a compression plant will range from $75 downward per 1000 cu. ft. of gas handled. The unit system should always be used in design so that the size of the plant can be increased or decreased without seriously interfering with the part in operation. Two or three compressors, tanks, or traps to do a given amount of work are better than one large one of equivalent capacity, provided the units are not so small as to be inefficient and uneconomic.

Buildings with steel framing covered with galvanized corrugated roofing are satisfactory. They should be well ventilated and there should be no low places in which the hydrocarbon vapors, which are heavier than air, can collect and form explosive mixtures. Doors should swing outward.

The main building should house nothing except the compressors. Other buildings should be 40 to 50 ft. away at least. Electrical wiring should be designed and put in with great care. Switches should be externally operated and all wiring should be in conduits. Safety lamps wired in accordance with the Underwriter's standard should be used. A well lighted plant looks better and is safer than one indifferently lighted. A small electrical generator should be part of the equipment of every plant, but neither the generator or any other small machine with rapidly moving parts should be housed in the compressor building.

The Absorption Process for Recovering Gasoline from Natural Gas.

The absorption process has been used in an extensive way only since 1915. At the present time one-quarter of the natural-gas gasoline marketed is made by this process in its various forms. According to Peterson [16] the method was first applied in the natural-gas industry at compressing stations on the gas lines transporting natural gas from the fields to centers of consumption. The use of an absorbent "dried" the gas and eliminated the line drip that accumulated in the low places. The process has developed rapidly, and is used to treat gases containing the gasoline hydrocarbons in such quantity that less than one gallon of condensate per 1000 cu. ft. of gas is obtained by the compression process. Gases from which 1.0 to 0.1 gallon or even less of gasoline is obtained can be treated profitably by absorption methods. However, the process

[16] *Trans. Am. Inst. Min. Eng.*, 1918, 2078-9.

is not limited in its application to the lean gases, but may be used to treat the richer gases.

The absorption process consists in bringing the natural gas into contact with a distillate or oil at as low a temperature as is economically possible, and at pressures ranging from a few pounds to several hundred pounds gage. The hydrocarbons of the gas and of the distillate or oil are mutually soluble. The result is the formation of a liquid phase that is rich in the higher hydrocarbons of the gas, and a gaseous phase consisting mainly of methane, ethane and propane. If a heavy oil is used as an "absorbent," it is distilled after having been in contact with the gas, and absorption gasoline is obtained as a valuable volatil product.

The scientific principles on which the process in its various modifications is based have long been known, and have been applied previously to the recovery of by-products in coke-oven plants and in several other industries. From the theoretical standpoint the absorption process consists in bringing a complex hydrocarbon gas into intimate contact with a liquid composed of substances that are soluble in hydrocarbons, and in which hydrocarbons are soluble. The time of contact must be sufficient to establish equilibrium or to allow a large part of the adjustment of phase compositions to occur. A liquid composed of high boiling hydrocarbons, yet not so viscous as to cause difficulty in handling, is frequently used as the "absorption medium." Octane, heptane, hexane, pentane, butane, propane, ethane, and methane are all soluble in this heavy hydrocarbon liquid, but in proportion decreasing with decrease in molecular weight of the hydrocarbons. If natural gas and an hydrocarbon oil are brought into intimate contact for a sufficient period of time, equilibrium, a condition independent of the further passage of time, will be established, and a new liquid-phase and gaseous-phase will be formed. Most of the octane, heptane, hexane, pentane and butane will be found in the liquid phase, and most of the methane, ethane and propane in the gas phase. The phase compositions will be found to vary with temperature and pressure. The lower the temperature and the higher the pressure the larger the proportion of all hydrocarbons in the liquid phase. The absorption process, therefore, from a practical standpoint, resolves itself into the selection of a suitable absorption medium, and in bringing gas and liquid into intimate contact for a limited period of time at the lowest temperature and highest pressure that can be economically used. The various practical limitations are referred to in the discussion that follows shortly.

The principle that the solubility of a gas or vapor varies with pressure is commonly known as Henry's law. The statement of this law will be found in any of the reference books or texts of physics or theoretical chemistry. Smith[17] states it, "The concentration of the saturated solution of any gas is proportional to the pressure at which the gas is supplied." The word "gas," of course, includes "vapor."

[17] *Inorg. Chem.*, 3d Ed., 188.

Washburn [18] states the law mathematically as $P_A = K_A X_A$ in which X_A is the mol-fraction of the solute species, A, K_A a constant that is characteristic of the solute A and of the thermodynamic environment which surrounds it in solution, and P_A the partial vapor pressure of the solute A in a dilute solution.

Henry's law holds rigorously only for dilute solutions of perfect gases in non-associated solvents. The hydrocarbon system involved in the absorption process is not of this type, and the relationship between pressure and solubility for any single gaseous hydrocarbon is far from linear. Furthermore, the hydrocarbons cannot be considered individually. The exact state of the system under any given set of conditions depends on the proportions of each substance in both phases. As in the compression process, mathematical calculation of the condition of the system is quite out of the question in the present state of our knowledge. The general scientific principles are useful only as qualitative guides.

Absorption Media.

The substance used as an absorption medium should possess the following properties:

1. Gasoline hydrocarbons shall be readily soluble in it.
2. Distillation range preferably 450 to 650° F. If lower boiling than this, a portion of the oil will be found in the product causing it to be off-color and of high end-point. The high boiling oils are unstable and form decomposition products of bad odor. Hence it is better to avoid the presence of large proportions of oil boiling over 650° F. The viscosity of oils containing large quantities of the higher hydrocarbons is higher than is desirable because of extra power consumption in pumping, and of poor distribution in the absorption tower.
3. The lower the viscosity the better, provided the distillation range is suitable.
4. The oil must not emulsify readily with water if steam-distillation is to be used in separating the gasoline.
5. The oil must not be easily oxidized, for compounds will be formed that cause emulsification and bad odor.

Various refiners make oils, cut between the heavy kerosene and ght lubricating oils, that will be found suitable for use as absorp- s.

ddition to the use of heavy oils there are instances in which s will be used as absorption media. Obviously lean gases would brought into contact with relatively volatil naphthas, for this in saturating the large volume of gas with the valuable of the naphtha, while at the same time hydrocarbons from the gas. But rich residual gases from weather- tail-houses, and some compression plants, may be with naphtha.

vsical Chemistry," 2d Ed., 181.

Plant Equipment and Operation.

Plant equipment includes absorbers, cooling coils, heat interchangers, steam-still, fire-still or pipe-still, condensers, and accessory apparatus. These several apparatus are discussed in Chapters IV, V, VI, and VII. The material of these chapters will be found directly applicable to the recovery of gasoline from natural-gas by absorption. Only a few special points will be mentioned in the paragraphs that follow. For data on current practice and numerous details the reader is referred to Bulletin 176 "Recent Developments in the Absorption Process for Recovering Gasoline from Natural Gas," Technical Paper 263 "Design and Operation of a Low-pressure Absorption Plant," and Technical Paper 232 "Absorption as Applied to Recovery of Gasoline Left in Residual Gas from Compression Plants," all published by the U. S. Bureau of Mines and obtainable at a very small cost.

Temperature and Pressure.

The temperature of the absorption medium should be as low as is economically possible, and surely not above 70° F. The vapor-pressure of the heavy-oil gasoline solution increases rapidly with increase in temperature, and for this reason provision should be made to cool the oil-gasoline mixture as it descends through the absorption column if the temperature increases more than 5 to 10° F. The temperature of the oil leaving the tower may be lower than that of the oil entering if the temperature of the gas entering the tower is lower than that of the oil. In this event every effort should be made to cool the absorption-oil more effectively in order fully to take advantage of the low gas temperature.

If calculation is made to determine what the temperature of the oil leaving the absorption column should be, if perfect interchange of heat between oil and gas is assumed, it will be found that the observed temperature of the oil will be higher than the calculated. The addition of heat in the absorber is the result of the liberation of the latent heat of vaporization of the gasoline as it passes from the gas-phase to the liquid-phase. This increase may be as much as 25° F. By the use of cooling-coils within the absorber the heat can be removed, and the per cent of gasoline in the oil-gasoline mixture increased accordingly. An increase from 6 per cent to 8 per cent in the gasoline content of this mixture means that 25 per cent less oil need be pumped, distilled, and passed through the system of heat-exchangers. Offsetting the saving in power and fuel in some degree is the cost of pumping the water in the absorber cooling coils.

The pressure under which the absorption medium and the gas are brought in contact should be the highest that can be economically used. In practice pressures varying from practically atmospheric to 500 lbs. per sq. in. are in use. The lean gases issue from the wells under high pressure, and advantage should be taken of this as far as possible. It is uneconomical to compress large volumes of lean gas to high pressures

merely for the purpose of conducting absorption operations under the higher pressure. If the gas is not obtained from wells under high pressure it will ordinarily be treated under the pressure required to move it through the gathering and distribution systems. The design of absorption towers is determined by the working-pressure, for the volume of the gas depends on the pressure.

Absorption Apparatus.

The gas coming to the plant is passed through some form of baffled trap or tower to remove dirt and scale, through water-cooled coils in which the temperature should be reduced below 70° F., and then into the absorber.

The commonest form of absorber is a packed tower. Whatever the apparatus may be, it must provide intimate contact between the gas and liquid phases for an interval of time sufficient to obtain an economical "saturation." Mechanical agitation for bringing oil and gas into contact has been tried, but no scheme of this nature can be satisfactory when a large volume of gas is to be intimately mixed with a relatively small volume of liquid. The success of any method depends on the creation of a large surface wetted with the liquid, and on the countercurrent movement of gas and liquid. Unless the liquid is completely frothed the surface produced by agitation will not be comparable in extent to that in a properly packed tower in which the liquid is well distributed. Countercurrent flow is also more easily obtained in the packed tower.

Absorption towers are usually 30 to 40 feet in height and 1 to 10 ft. in diameter. The thickness of the walls depends on the working pressure, and it is not customary to build towers of diameter greater than 30 inches if the working pressure is 200 pounds and upward. As in the compression plant, it is better to have several units of moderate size than one or two of large size.

Wooden grids, broken bricks, stones, tiles, steel cuttings, and various other materials have been used as tower packings. This subject is discussed in Chapter VII. A packing material should present a large surface that can be wetted with liquid, and at the same time allow a maximum "free-space." Metal cylinders of about the same diameter as length are as good as any other easily obtained filling material, and far more effective than bricks, tiles, or wooden grids. The size of the tower, the quantity of solid matter suspended in the liquid determine the diameter of the cylinders, or rings as they are usually called. Rings of 1-in. to 1½-in. diameter are suitable for use in absorption towers. The tower should be divided into sections, and each of these filled with rings. Otherwise the weight of the filling will crush the rings in the lower part of the column. In some instances the iron may be attacked by the oil as a result of the presence of organic acidic substances, but this can be avoided by properly selecting the absorption oil, or by the use of special thin cast-iron packings.

A tower packed with wooden grids is described by W. P. Dykema and A. A. Chenoweth.[19] The grids are made from smooth wooden strips, $5/8$ in. x 4 in. in cross section, set on edge and spaced $5/8$ in. apart. The lower edge of each strip is notched by a saw kerf $3/16$ x $3/16$ in. in order to prevent the oil from travelling to the ends of the strips and thence to the walls of the tower. Excellent distribution of the oil is reported.

A tower packed with wooden grids of this sort can never be as effective, volume for volume, as one packed with rings, for the free space is only about 50 per cent as compared to about 95 per cent for the rings, and the surface is also very much less.

Gas-velocity and Oil Circulation.

The variable factors in tower operation are temperature, pressure, gas-velocity and rate of oil-circulation. With temperature and pressure determined, the problem resolves itself into adjusting the rates of gas and oil flow for efficient recovery of gasoline and economical operation.

Dykema reports gas velocities ranging from 30 to 260 ft. per minute in the various plants inspected, but in most instances the velocity was between 35 and 75 feet per minute. No general rule can be given for determining what gas-velocity should be, for it depends on the other variable factors in a manner not yet determined. But one should prefer to err on the side of safety, since the gasoline lost in a very short time would pay for the additional absorber capacity required. The lower the pressure under which the tower operates the slower the gas should travel. The gas-liquid system is farther from a condition of equilibrium when the pressure is high, and hence makes part of its adjustment toward equilibrium more rapidly than if the pressure were low.

The rate of circulation of oil and the rate of gas flow are to some extent interdependent. The loss contingent upon too rapid gas-flow can be avoided in some measure by largely increasing the quantity of oil circulated in unit time, but this would be an expensive remedy.

Sufficient oil must be circulated to thoroughly wet the surfaces of the tower filling, and to obtain a gasoline-oil solution from the bottom of the tower that contains at least 5 to 10 per cent of recoverable gasoline. The actual results obtained with a given plant equipment depends on gas composition, as well as on the other factors mentioned. Hence, it is desirable to experiment with the plant in order to determine the best combination of gas-rate and oil-rate. Increased yields should always be compared with the increases in cost necessary to obtain them. On the one hand the less the quantity of oil that can be used the less the pumping and fuel costs, but on the other, the less the oil circulated the more likely the loss of valuable hydrocarbons in the gas.

[19] U. S. Bur. Min., Tech. Paper 263, 6-7.

Distillation of the Oil-gasoline Solution.

The oil-gasoline solution from the absorption column should be pumped directly to the still. If flexibility is desired at this point in the process the oil may be run to a tank and pumped from the tank to the still. The use of a weathering tank in which the oil-gasoline solution is held until much of the dissolved gas has been evolved is absurd. The still, if properly designed, is an excellent weathering device, for not only will the gases be evolved but they will be washed by, and nearly brought into equilibrium with, the gasoline. The sharpest separation of the gaseous and most volatil hydrocarbons from the salable gasoline will be effected.

The gasoline may be separated from the heavy oil solution by steam-distillation, or by the use of continuous topping apparatus such as pipe-still and evaporating chamber. Emulsification of the heavy oil with water is avoided if steam is not used in the distillation, but emulsification need not be a serious problem if the absorption oil is carefully chosen. The sweetening effect of the steam is desirable. Small amounts of hydrogen sulfide and other odoriferous impurities are dissolved in the water formed as the steam is condensed.

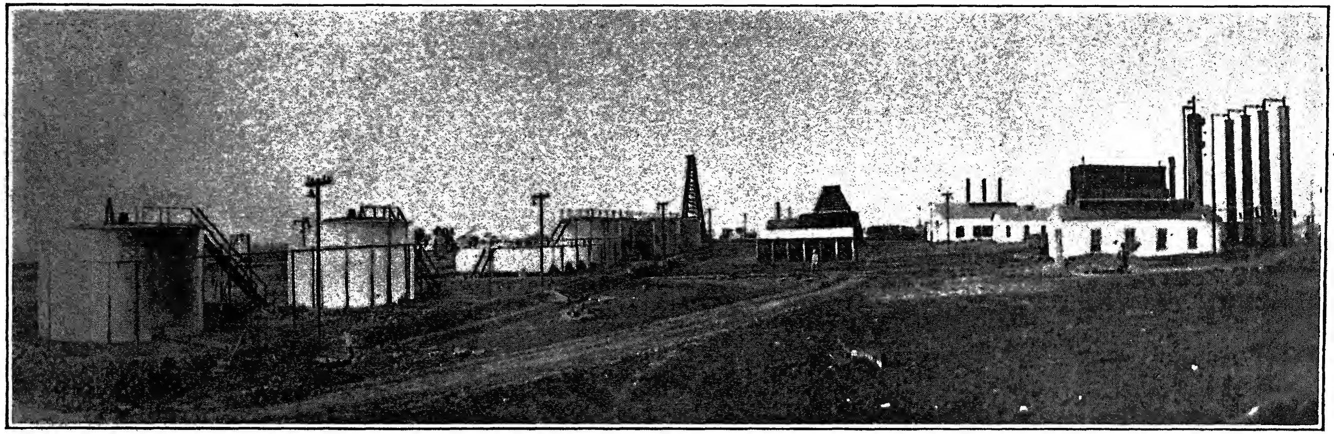
A continuous steam-still needs consist only of an efficiently packed column 30 to 40 ft. in height. The large tank or still often observed as part of "steam-still" is unnecessary.[19a] Provision must be made for the continuous introduction of the gasoline-oil mixture, and the required amount of steam (largely exhaust steam if steam rather than power-pumps are used), should be introduced at the base of the column. Oil and water are continuously removed from the bottom of the column. The column should be provided with a suitable reflux and condenser.

The hot effluent oil is separated from the water and passed into a heat exchanger in which it gives up heat to the gasoline solution on its way to the column. The "stripped" and somewhat cooled absorption oil is then pumped through pipe-coil coolers, and, with its temperature reduced to 60 to 70° F. or lower, is again ready to be pumped to the absorption tower.

The Merriam process [20] plants use no steam in distillation. This avoids emulsions and allows of the use of cheap oils for absorption. No boiler equipment is required. The claim is made that the method is very economical, and the only one that can profitably treat 50,000 to 250,000 cu. ft. of gas that is not rich in gasoline.

An absorption plant of novel appearance is the Bertsch process plant of the Skelly Oil Company near Slick, Oklahoma.[21] The physical principles are the same as in any absorption plant, but the apparatus used is of rather startlingly novel appearance. The claims to unusually economical operation are based on the fact that no boiler or pumps are used, and that the operating-pressure is low.

[19a] See context of Chapter VII.
[20] See booklet published by The Superior Oil and Refining Company, Columbus, Ohio.
[21] See *Nat. Pet. News*, Mar. 29, 1922, 43.

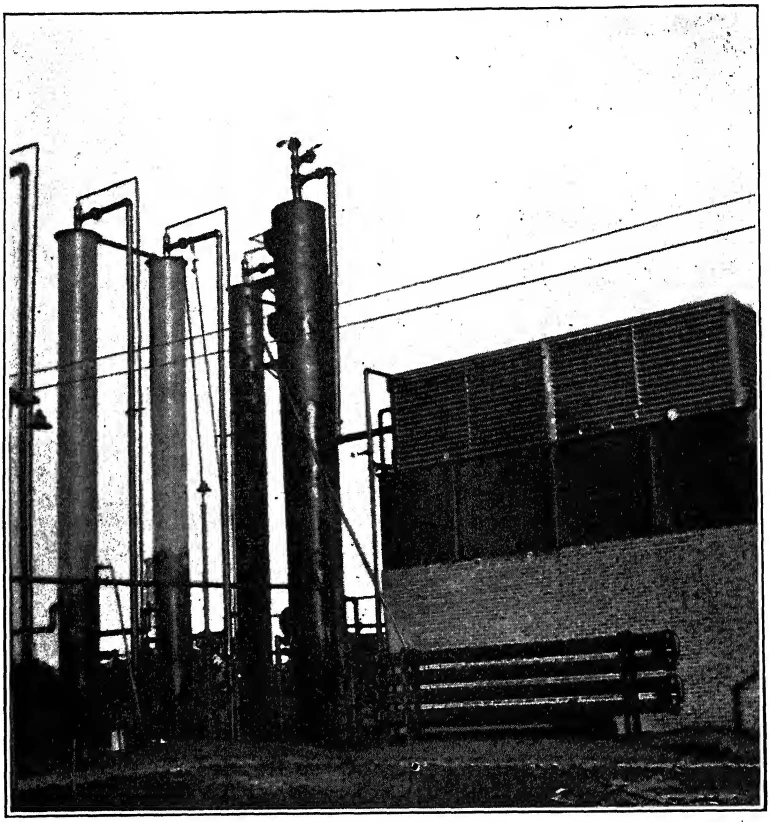


Courtesy of Dr. C. M. Alexander.

FIG. 131.—Absorption Plant of the Plateau Oil Company at Breckenridge.

Description of a Low-pressure Absorption Plant.[22]

The plant of the Plateau Oil Company at Breckenridge shown in Figures 131 and 132 is interesting as an example of what is being done in the way of low-pressure absorption. This plant was designed,



Courtesy of Dr. C. M. Alexander.

FIG. 132.—Absorption Plant of the Plateau Oil Company, Showing Absorbers, Steaming Column, Heat-Exchanger, Pipe-Coil Condenser, and Box-Condenser.

erected, and put in operation by the Bostaph Engineering Company. The cost of plant and gathering lines was approximately $150,000.00 (1920). Seven million cubic feet of gas are handled daily.

Ten to fifteen pounds pressure is held on the wells by means of

[22] I am indebted to Dr. C. M. Alexander for the detailed description of this plant.

pressure control valves on the gas-separators. The gas reaches the plant at 5 to 10 lbs. gage pressure, and passes into the bottom of the absorbers. These are vertical cylindrical tanks 3 ft. in diameter, 40 ft. high, and filled with wooden grids. The oil is introduced at the top of the absorber, and leaves at the bottom as a hydrocarbon solution containing 6 to 7 per cent of gasoline. This mixture is pumped into the top of a continuous steaming column 4 ft. in diameter, 40 ft. high, and filled with ordinary house tile. The vapor from the steaming-column enters primary condenser coils that are sprayed with water and that are provided with back traps from which condensate is returned to the column as from the reflux of the conventional column-still. The vapor from the primary condenser coils enters the submerged coils of a box-condenser. The hot oil from the bottom of the steaming column is passed through an heat-exchanger so that a portion of the heat is transferred to the oil-gasoline mixture entering the top of the column. The steam used for distillation is mainly that exhausted by the pumps.

The gasoline obtained ranges from 65 to 70° Bé., and is absolutely water white. No re-running is required. If more oil was circulated through the absorption column a 74 to 76° Bé. product, such as is usually obtained in absorption plants, could be made; but at present the lower gravity product, salable directly as a motor-fuel, is desired. The daily yield of 65 to 70° Bé. gasoline is 5000 gallons, or 0.71 gallons per 100 cu. ft. of gas.

Boosters are to be added to the equipment of the plant so that the absorption will take place under 50 to 75 lbs. pressure. This is expected to result in obtaining a higher yield.

The operation of the plant requires the services of a superintendent and four shift men, two on each 12-hour shift.

Descriptions of several other plants will be found in the Bulletins and Technical Papers of the U. S. Bureau of Mines.

Comparison of Compression and Absorption Processes.

The quoted and tabulated sections that follow are those of Mr. F. P. Peterson,[23] and, at the time they were written, in my opinion, a fair statement of the relative merits of the two processes.

"A comparison of the relative merits and details of the two systems of operation will be of interest. A clean-cut and exact comparison cannot be made of all the features to be considered, since, as stated, the absorption system is considerably behind the compression system in its present stage of development as against its anticipated possibilities. Enough can be seen, however, to indicate that the two systems operating in competition will be fairly evenly balanced with reference to operating cost, and when all refinements are applied in either case, it is the writer's judgment that the compression system will be found preferable."

[23] *Trans. Am. Inst. Min. Eng.*, 1918, 2082-84.

Compression System.	Absorption System.
"(a) System is now well standardized. Gas-engine power equipment and compressors designed especially for the work are available. The range of operating pressure is also standardized and definite estimates and plans for development are a simple matter.	"(a) System not so well standardized. In fact, is in process of development and evolution to working standards.
"(b) Condensing equipment, such as oil separators, condenser coils, accumulators and various details are well standardized.	"(b) In absorption systems corresponding details are not yet developed to approach acceptable standards. Absorbers of about three distinctive types are exploited. Some details of refinement are to be worked out with reference to absorbent circulation that offer no apparent difficulty of solution.
"(c) Operation requires skilled attendants familiar with the handling of gas compressors operating to 250-lb. gage pressure.	"(c) Practically the same limits obtain in absorption as in compression with exception that it appears likely that standards of operating pressure will be very materially lowered by comparison.
"(d) Skilled and experienced attendants are required to handle a very volatil product. Treatment known as 'weathering' involved. Use of steam required during cold weather. Storage of unweathered manufactured product requires especially constructed tankage.	"(d) Steam boilers and stills required to be maintained in continuous operation. Product as afforded by methods developed to present date less volatil than in compression system. Storage tankage of a cheaper class is being used. It is most likely, however, that improvements or further refinements in absorption system will bring about condition parallel to compression system in nature and volatility of product. This development will follow because of possible increase, by such development, of sufficiently greater output to justify such refinement.
"(e) Gas must be treated under artificial pressure.	"(e) Gas may be treated under natural well pressure.
"(f) Additional machinery almost invariably used for producing vacuum.	"(f) It has not yet been determined that vacuum applied to gas wells not producing oil can be profitable.

Compression System.	Absorption System.
"(g) Compressor system admirably adapted to rich casing-head or oil-well gases.	"(g) Absorption system adapted to dry gas or oil-well gases of lean saturation.
"(h) Investment for plant equipment, required under most favorable conditions, basis of 500M. cu. ft. unit capacity gas treatment, approximately $30,000. In terms of manufactured product per unit barrel of 50 gal., above figure will reduce to $428.	"(h) For comparison of most favorable conditions for 500M. cu. ft. unit capacity $15,000. In terms of manufactured product per unit barrel of 50 gal., above figure will reduce to $1000.
"(i) Maintenance and upkeep, depreciation, insurance and taxes, classify about as oil refinery operation.	"(i) Comparable to compression.
"(j) Over-all extraction recovery efficiency admittedly short of possible recovery by margin amounting to from $\frac{1}{8}$ to $\frac{5}{8}$ gal. per 1000 cu. ft. unless tail-gas refrigeration be used, adding about 20 per cent to cost.	"(j) System should attain practically 100 per cent recovery of extraction product, provided steam-stills are operated under pressure or small compressors be employed for liquefying light steam-still production. This application has not been generally made to date. It may be assumed that the loss due to escaping light products is greater than the admitted loss or inefficiency of the compressor system. Corrective measures can be applied at a cost within 10 per cent of total investment.
"(k) Value of manufactured product 18¢ per gallon in blended state. Operation of blending at plant adds 15 to 25 per cent to over-all efficiency as against operation in which blending is carried on separately.	"(k) Product usually sold unblended. Value for comparison, 20¢. Direct comparison of values under this designation cannot be analyzed until more is known from practical results of operation wherein all refinements are embodied.

"Costs of operation involving salaries of attendants, lubricants, waste, and plant supplies will be about equal.

"In the case of the simple battery of absorption equipment with a recovery-still interposed in a pressure gas-main, the skill required on the part of the plant operatives may be less than in the case of a compression plant involving all its branches and details when developed to the full extent. It is also likely that a greater degree of skill on the part of attendants will be required for absorption operation in which

vacuum and compression are also used, for the reason that the details of operation are somewhat more extended. However, this difference will not be material.

"It will be understood in this connection that the absorption system is being exploited in competition with the compression system for the working of rich casing-head or oil-well gases, and when so applied practically all of the refinements and ramifications of the compression system are involved and the only material advantage to be gained is the possibility of operating on gases with a wide variance of saturation with one and the same system without results detrimental to the yield from the rich gases by presence of the lean gases in preponderance."

During the last four years the absorption process has been improved in an engineering way. More regard has been paid to fundamental physical principles, and to economy in operation. There has been a notable tendency to build absorption plants for handling the richer gases. Standardization and more intelligent design of equipment has led to lower plant investment and operating costs. As I have pointed out there is still much room for improvement.

The product currently made in absorption plants is less volatil than that of the compression plants. The gravity of the usual absorption gasoline of today is 72 to 76° Bé., while compression condensate runs 80° Bé. upwards. As Mr. Peterson suggests there is no inherent reason when the two methods should produce different products if the plants using each were correctly designed and efficiently operated.

All in all, I am of the opinion that the absorption method at its best is to be preferred to compression. However, it is unwise to generalize, for local or special conditions may be of the greatest importance in making a choice. The standardization of the compression process, and the expert technical guidance and service available to the purchaser of equipment for a compression plant should commend this method to the inexperienced operator.

Treating Residual Gas by Absorption.

The residual gas from compression plants can be very profitably treated by absorption for recovery of the gasoline not removed by compression and cooling. As I have already pointed out, the impression that residual gas from compression plants, and gases formed on weathering, contain only the volatil or "wild" hydrocarbons is erroneous. The residual gases from compression plants, from weathering operations as ordinarily conducted, or from refineries, can be brought into intimate contact with naphtha, or with an heavy oil, for the recovery of their content of valuable gasoline. This subject is discussed by Dykema and Neal in Technical Paper 232 of the U. S. Bureau of Mines, and descriptions and photographs of several plants are given. A recent serial[24] of the U. S. Bureau of Mines by D. B. Dow treats of the recovery of gasoline from uncondensed still vapors. Gasoline recovered in this

[24] No. 2344, April, 1922.

way must be refined to remove H_2S by washing with alkali. This is of special importance in gasoline recovered from cracking-plant gas.

The Adsorption Processes for Recovering Gasoline from Natural Gas.

The fact that the molecules of suitably prepared surfaces of solid substances possess the property of combining in some manner with the molecules of gaseous or liquid substances has long been recognized. The phenomenon is called *adsorption* to distinguish it from mechanical processes such as the taking up of water by a sponge, which process is referred to as absorption.

A familiar example of adsorption is combination of the molecules of gases with the surface of an active charcoal. So energetic is the process that it has been used frequently in the laboratory for the production of vacua as high as 0.001 mm. of mercury. The removal of dyes from aqueous or alcoholic solutions by means of bone-black, and the lightening of the color of oils by percolation through fullers' earth are familiar examples of selective adsorption.

The subject of adsorption and surface phenomena in general is one on which much has been written, and in which great interest is shown at present. Many phenomena that, to preserve dignity and cover ignorance, have been shelved in that category of profound, yet evasive name —catalysis—will be readily explained when we know more of surface energy. The reference works on theoretical chemistry should be consulted on the subject of adsorption and surface energy. Recent papers of Harkins, Langmuir, and others, for the most part published in recent volumes and numbers of the *Journal of the American Chemical Society,* treat of the newer discoveries in this field of physical and chemical science.

The Charcoal Adsorption Process.

The gasoline hydrocarbons of natural gas, under proper conditions, can be selectively adsorbed by activated charcoal, and subsequently recovered from the charcoal by distillation with steam. This process in its commercial aspects is a development of the last five years. The patents are controlled by the Gasoline Recovery Corporation of Charleston, West Virginia. Drs. Burrell and Oberfell, formerly of the U. S. Bureau of Mines, are associated with this corporation and have published [25] a preliminary description of the process.

When natural gas containing gasoline hydrocarbons is passed through activated charcoal the hydrocarbons are adsorbed with liberation of heat. On account of the chemical similarity of the lower paraffin hydrocarbons it would hardly be expected that the adsorption would be highly selective, that is, that all of the pentane, hexane, and heptane would be adsorbed to the exclusion of the hydrocarbons of lower molecular weight. But the gasoline hydrocarbons are somewhat more readily adsorbed than those of lower molecular weight, and if the gas

[25] *Chem. Met. Eng.,* 24 (1921), 156-60.

is passed through the charcoal for some time after the period in which heat is rapidly evolved, the methane, ethane, propane, and butane are largely displaced by the higher hydrocarbons.

The flow of gas is then stopped and the charcoal is heated with steam. It was formerly thought that superheated steam was required, but it has been found that saturated steam can be used. The gasoline is not completely removed from the charcoal, but the part remaining does not interfere with the further use of the charcoal. The process can be applied at any pressure.

The charcoal-adsorption plant consists of adsorbers, steam-boilers, condensers, and storage tanks. The adsorbers are used in sets of three, of which one is treating gas, one being distilled with steam, and the other cooling. Each adsorber, in its turn in the operating cycle, is used to treat gas.

The method is as yet in the developmental stage, although several commercial plants have been built. The advantages of the process as stated by Oberfell and Burrell[26] are as follows:

"Cost of construction—fewer units and less expensive apparatus are required than in other processes.

"Yield—the yield of gasoline is 100 per centum. Not a fraction of a pint of gasoline escapes.

"Quality of product—the product obtained from the charcoal process is superior in gravity, vapor tension and odor to that produced by other methods.

"Pressure—the charcoal process operates efficiently at any pressure. The writers are at present operating a plant at one and one-half-pound pressure.

"Size of installations—the charcoal process lends itself efficiently either to large or small installations on 'dry' or casinghead gas.

"Wastage—there is no wastage of charcoal in the operation of a plant as there is of oil in an oil absorption plant. One charge lasts indefinitely and actually becomes more efficient with use.

"Moving parts—there are no moving parts in the charcoal process to become out of order except gasoline and water pumps. There is no high pressure apparatus (unless a high pressure gas is being treated) to get out of order."

There is no doubt but that the product made by the charcoal process is excellent. A gasoline of 85° Bé. will have a "vapor pressure" of about 5 lbs. per sq. in. Yet, as a result of the presence of a large proportion of pentane, some 15 per cent more of charcoal-process gasoline than average absorption gasoline will distill under 100° F. The loss in distillation will be as low as 5 to 8 per cent.

The process has interesting future possibilities. For further details and also for discussion of the general theory the references given below[27] may be consulted in addition to those cited above.

[26] *Pet. Mag.*, June, 1920, 60.

[27] Voress, C. L., *Oil Age*, 17, Sept., 1921, 38-40. Anderson, R. P., in Day's "Handbook of the Petroleum Industry," Volume I, 744-51. Harkins, W. D.,

Numerous further references to the literature will be found in these articles and those cited in the context.

The Silica-Gel Process.

The silica-gel process depends on the adsorption of the gasoline hydrocarbons by a very porous form of silica. The name suggests that the material is used in the form of a colloid gel, but, in fact, it is hard and glassy and of the appearance of fine quartz sand. At one stage in the manufacture of the adsorbent the silica is in the form of a gel. The name is derived from this. The silica-gel process is controlled by the Silica Gel Corporation, a subsidiary of the Davison Chemical Company of Baltimore. Descriptive bulletins can be obtained from the Silica Gel Corporation. The theory of the process is discussed by E. B. Miller.[28] This process, like that in which charcoal is used as an adsorbent, presents great possibilities, and its commercial development will be followed with keen interest.

Effect of Gasoline Removal on the Heating Value of Natural Gas.

The supposed loss of heating value resulting from the removal of gasoline has caused many controversies to which public utility commissions and legislative bodies have been parties. No argument is in truth involved, for the answer to the question is a matter of fact, determinable either by calculation alone, or by experimental investigation. The U. S. Bureau of Mines has shown that the loss in heating value of the "dry" gas ordinarily supplied to the domestic consumer is about 2 per cent. Treatment of the very rich or "wet" gases results in losses of 5 to 25 per cent, but the residual gas in these instances will have heating values of 1200 to 1700 B.t.u. per cubic foot which is higher than the heating values of untreated dry gases.

Gases of high heating values are not effectively utilized in the domestic appliances used to burn them. Heating values of 1000 to 1100 B.t.u. are surely the maximum desirable. It is therefore clear that no argument is involved. In fact the treatment of the gases for the removal of gasoline is a benefit rather than a loss. The difficulty caused by condensation of hydrocarbon liquid and water at various points in the distribution system is avoided, and it is thus unnecessary to waste gas in blowing out traps or drips. Rubber gaskets in couplings are not attacked, and leakages are therefore less frequent, and pressure variations are less annoying.

The reader should refer to Technical Paper 253 of the U. S. Bureau of Mines (1920) for a detailed discussion of this subject, and for numerous references to the technical literature dealing with various questions involved.

and Ewing, D. T., *J. Am. Chem. Soc.*, 43 (1921), 1787-1803. Liesegang, R. E., *Chem. Ztg.*, 44 (1920), 89-90. A review of the literature from 1914-1919 on carbon as an adsorbent. Berl, E., and Andress, K., *Z. Angew. Chem.*, 34 (1921), 369-71, 377-82.

[28] *Trans. Am. Inst. Chem. Eng.*, 13 (1920), 379-411.

Sulfur in Natural-gas Gasoline.

Natural-gas gasoline from a few districts contains hydrogen sulfide and possibly other sulfur compounds that give it a bad odor. In the Lawrenceville district of Southern Illinois, and at a plant in the Santa Maria field and another in the Salt Lake field in California the natural gas was so corrosive that the pipes of the cooling coils were eaten through in 3 to 6 months. The corrosion was most rapid in the lower part of the coils. The compressor was not corroded. The condensate produced in the Illinois plant contained sulfur, but that made in the California plants did not contain enough sulfur to cause trouble.[29] From these facts it appears that carbon dioxide as well as H_2S may have been responsible for the corrosion.

Natural-gas gasoline that contains sulfur and will not pass the doctor test is somewhat difficult to market. The refiners' finished gasoline will contain 10 to 15 per cent of the natural-gas gasoline. If the refinery stock passes the doctor test, the addition of 10 to 15 per cent of a natural-gas product that does not contain much sulfur will not result in a final product showing a positive doctor test. However, it is much better to market a natural-gas gasoline that can be guaranteed to pass the doctor test. A gasoline of this nature rightly commands a premium of 1 cent or more in the market.

The U. S. Bureau of Mines [30] has investigated methods for producing natural-gas gasoline that will pass the doctor test. The less volatil portion of the gasoline was found to contain more sulfur than the more volatil part. Washing the gasoline with a sodium plumbite solution, made from a 20 per cent caustic soda solution by adding 7 per cent of litharge and 2 to 3 per cent of powdered sulfur, produced a sweet gasoline. One part of this solution was sufficient to sweeten 200 parts of very sour gasoline. After treatment with the plumbite solution it is necessary to wash the gasoline with water to remove the yellow color formed as a result of the plumbite treatment. The Bureau found that the refining was effectively done when the gasoline was introduced at the bottom of a tower-scrubber filled with a packing material and the plumbite solution. A similar procedure was effective in washing with water. The water must be changed about five times as often as the plumbite solution. No final recommendations are made by the Bureau, [illegible]s quite apparent that a continuous scrubber or treating apparatus [illegible]e easily designed. At one plant [31] in California a water scrub[illegible]ed both to condense the hydrocarbons and refine the con-

H. W. Young and A. W. Peake [32] of the Mid-West Refining Company have described methods used by this company in sweetening natural gasoline blend. The natural gasoline is a compression plant product made in the Salt Creek field, and is blended 50:50 with a

[29] U. S. Bur. Min., *Bull. 151*, 56-7.
[30] Ser. 2191, Dec., 1920, by D. B. Dow.
[31] See U. S. Bur. Min., *Bull. 151*, 57-8.
[32] *Chem. Met. Eng.*, 27 (1922), 972-6.

naphtha topped from the crude in the refinery at Casper. Both the natural gasoline and the naphtha are sour.

The use of sodium plumbite and sulfur for sweetening is not regarded favorably at the Salt Creek gasoline plant because of the very large quantity of water required for washing to remove the color caused by treatment with the doctor solution. Steam distillation of the treated blend involves a heavy expenditure for equipment and would be a serious drain on the meager water supply.

The objectionable sulfur compounds were believed to be mercaptans because the blend was rendered permanently sweet when treated with solutions containing silver or mercury complex ions. The treating process finally developed consisted in bringing the sour distillate into contact with a solution of bleaching powder containing 50 to 75 pounds of bleach in each 2000 gallons of solution. Bleach was used rather than liquid chlorine because of the cost of transporting the cylinders in which the chlorine is shipped. In experimental work, it was found that ½ lb. of bleaching powder with 30 per cent available chlorine would sweeten 225 gallons of blend.

The treating plant consists of five steel cylinders each 6½ ft. in diameter and 20 ft. high. The vapor-pressure of the blend is reduced to 42 lbs. in the first cylinder. The blend then flows to the second cylinder through a "knothole" mixer, and passes upward through about 5 feet of bleach solution. The "knothole" mixer consists of a pair of companion flanges between which is a disc punched with a many-pointed star-shaped hole. The eddying flow caused by passage of the liquids through this irregularly shaped orifice effects so good a mixing that the treatment occurs largely during the brief interval of mixing.

From the tank containing the treating solution the blend passes to the washing tank where it is washed with water, and then to a settling tank and to storage. The consumption of bleach is about 2.75 lbs. per 1000 gallons of blend. This is a somewhat higher bleach requirement than was indicated in the preliminary tests, the increase probably resulting from mechanical carrying of bleach solution from the treating tank to the wash tank. The plant is handling 75,000 to 85,000 gallons of blend daily, and probably could treat twice this quantity. A single shift-man runs the plant.

Several other points of interest are discussed in the paper. The problem of suitable materials of construction is being studied, but the corrosion of the iron and steel equipment was not unusually serious. Experiments were made at the Casper refinery to test the usefulness of hypochlorite refining of various products. Some heavy naphthas were treated successfully and economically, while others could not be handled at all. Lighter naphthas were refined successfully, but with a somewhat higher consumption of bleach than was required for the blend at Salt Creek. Young and Peake conclude that the hypochlorite treatment is not suitable for heavy naphthas, but that it is an economical and satisfactory method for refining and sweetening natural gasoline, or gasoline from steam- or fire-stills.

Specifications for Natural-gas Gasoline.

The Association of Natural Gasoline Manufacturers deserves much credit for the work done by it in drawing specifications for several grades of natural-gas gasoline. Four grades of "Natural" gasoline designated by letters A to D inclusive, and four grades of "Motor Natural" gasoline designated by numbers 1 to 4 inclusive, are now recognized.

The specifications adopted by the Association in 1921 recognized seven grades of natural gasoline. At the December, 1922, meeting, the number of grades was reduced to four. Grades A and B represent the products of absorption plants, and C and D those of compression plants.

In drawing specifications, the gravity, initial boiling point, end point, color, and recovery have been considered. The committee believes that the initial boiling point is too much affected by variations in temperature of the sample and room, and by manipulation, to be taken as the sole criterion of volatility. Hence, they include a specification for "recovery," meaning by this the percentage of the sample distilled that has collected in the receiver when the distillation is complete. Also, although it is not included in the specification, the analyst will be guided by the character of the distillation curve.

The Committee has eliminated the requirement for "vapor-tension" that was included in the 1921 specifications. This was done because of lack of a dependable and accurate method of determining "vapor-tension."

No requirements as regards sulfur content of natural gasolines are included in the specifications. This should receive consideration, as blended gasolines come on the market that are of bad odor as a result of H_2S, and possibly other sulfur compounds, contained in the natural gasoline used in blending.

The specifications adopted by the Association in December, 1922, are shown in Table LXV.

The color of all products must be water-white, plus 25 Saybolt chromometer. The distillation method of the American Society for Testing Materials shall be used, with the additional provision that the condenser water shall be at a temperature of 32 to 34° F. The receiving cylinder shall be surrounded with ice-water if necessary. The temperature of the condensate in the receiver shall be 55 to 65° F.

The terms "Natural Gasoline" and "Motor Natural Gasoline" cover the products formerly known as "Casinghead," "Absorption" and "Blends" which are now obsolete terms.

Mr. D. E. Buchanan [33] states that the most consistent test for the "stability" of natural-gas gasolines is to determine the per cent that vaporizes up to 100° F. This is the sum of the per cent of distillate collected up to 100° F. and the loss during distillation. This should not exceed 50 per cent for compression gasoline, or 25 per cent for absorption gasoline.

[33] *Nat. Pet. News*, Mar. 15, 1922, 32-C.

TABLE LXV

SPECIFICATIONS FOR NATURAL GASOLINES AND MOTOR NATURAL GASOLINES[34]

	NATURAL GASOLINE	
Grade A:	Gravity	Not below 72 Bé.
		Not above 78 Bé.
End point		Not over 375 F.
Recovery		Not less than 90 per cent.
Grade B:	Gravity	Not below 76 Bé.
		Not above 82 Bé.
End point		Not over 375 F.
Recovery		Not less than 88 per cent.
Grade C:	Gravity	Not below 80 Bé.
		Not above 88 Bé.
End point		Not above 350 F.
Recovery		Not less than 78 per cent.
Grade D:	Gravity	Not below 88 Bé.
		Not above 92 Bé.
End point		Not above 350 F.
	MOTOR NATURAL GASOLINE—BLENDS	
Grade 1:	Gravity	Not below 58 Bé.
		Not above 62 Bé.
End point		Not above 437 F.
Recovery		Not less than 91 per cent.
Grade 2:	Gravity	Not below 58 Bé.
		Not above 62 Bé.
End point		Not over 450 F.
Recovery		Not less than 90 per cent.
Grade 3:	Gravity	Not below 64 Bé.
		Not above 66 Bé.
End point		Not over 440 Bé.
Recovery		Not less than 88 per cent.
Grade 4:	Gravity	Not below 66 Bé.
		Not above 70 Bé.
End point		Not over 435 Bé.
Recovery		Not less than 85 per cent.

Storage, Handling, and Shipment of Natural Gasoline.[35]

The more quickly natural-gas gasoline can be marketed the better, for the less the loss. The storage capacity of the tanks at any plant will depend on the business relationships of the company operating the plant and on the general market situation. A plant making 1000 gallons of gasoline per day should provide storage for at least 100,000 gallons unless the product has an assured outlet.

[34] The name "Natural Gasoline" is used by the Association rather than "Natural-Gas Gasoline" and "Casinghead Gasoline." This usage appears desirable, but at present is somewhat confusing because of the synonymous use of "natural gasoline" and "straight run gasoline" by some writers.

[35] A paper with many practical suggestions was written for the meeting of the Western Pet. Ref. Assoc. at New Orleans, Mar. 8, 1922. See *Nat. Pet. News*, Mar. 15, 1922, 32C-32D.

Storage tanks should safely withstand 15 to 20 pounds pressure, should be located at least 75 to 100 feet from the plant and from the operating tanks, should be provided with pressure and vacuum relief valves connected to the residue gas line and with water-drain at the lowest point, and should be painted white or with a lacquer containing powdered aluminum pigment, or preferably should be insulated with a non-conducting material.

If the gasoline is off-color as a result of contact with oil or grease in pipes it may be rendered suitable for shipment by filtration through fullers' earth. A portable filter of 50 to 75 gallons capacity can be set on the dome of the tank-car. The outlet from the filter should be fitted with a metal screen and several layers of fine cheese cloth in order to prevent fine particles of the earth from passing into the car. Several hours are required for natural-gasoline to completely "wet" fullers' earth, and the earth does not function properly until it is thoroughly wetted.

Natural-gas gasoline and blends made therefrom are transported in various ways. Some are pumped under pressure through 2-in. pipe lines connecting the gasoline plant with a blending station or petroleum refinery. Auto trucks with pressure tanks are used in some instances for short hauls. In California and the Mid-Continent several large producers mix the gasoline with the crude oil on its way to the refinery through pipe-lines. Not only is volatilization loss thus prevented, but the viscosity of the oil in the pipe-line is somewhat reduced. The larger proportion of gas that is formed when this petroleum is distilled is handled by compression or absorption at the refinery.

The present regulations of the Interstate Commerce Commission for the shipment in tank cars of inflammable (red label) petroleum products are as follows:[36]

"All inflammable liquids must be shipped in packages complying with specifications that apply as follows:"

(j) In tank cars complying the Master Car Builders' specifications provided the vapor tension of the inflammable liquid corresponding to a temperature of 100° F. does not exceed 10 pounds per square inch. A tank car must not be used for shipping inflammable liquids with a flash point lower than 20° F., unless it has been tested with cold-water pressure of 60 lbs. per sq. in., and stenciled as required by Master Car Builders' specifications, and is equipped with safety valves set to operate at 25 lbs. per sq. in., and with mechanical arrangement for closing dome cover as specified in paragraph 1824 (k).

(k) Liquid condensates from natural gas or from casinghead gas of oil wells, made either by the compression or absorption process, alone or blended with other petroleum products, must be described as Liquefied Petroleum Gas when the vapor pressure[37] at 100° F. (90° F. November 1 to March 1) exceeds 10 lbs. per sq. in.

[36] Items from Sections 1824, 1825, and 1913, Bur. Exp., Pamphlet No. 9 as modified by Sup. 1, obtainable from the Bur. Exp., 30 Vesey Street, New York City.

[37] In measuring the vapor pressure the container may be vented momentarily at a temperature of 70° F.

When the liquid condensate alone or blended with other petroleum products has a vapor pressure not exceeding 10 pounds per square inch, it must be described and shipped as Gasoline or Casinghead Gasoline.

Liquefied petroleum gas of vapor pressure exceeding 10 lbs. per sq. in. and not exceeding 15 lbs. per sq. in., from April 1 to October 1, and 20 lbs. per sq. in. from October 1 to April 1, must be shipped in metal drums or barrels which comply with Shipping Container Specification Number 5; or in special insulated tank cars approved for this service by the Master Car Builders' Association.

Liquefied petroleum gas of vapor exceeding 15 or 20 lbs. per sq. in. as provided herein, and not exceeding 25 lbs. per sq. in., must be shipped only in metal drums or barrels which comply with Shipping Container Specification No. 5.

Liquefied petroleum gas of vapor pressure exceeding 25 lbs. per sq. in. must be shipped in cylinders as prescribed for compressed gases (see pars. 1861 to 1863, inclusive).

When the liquid condensate, alone or blended with other petroleum products, has a vapor-pressure not exceeding 10 lbs. per sq. in. it must be described as Gasoline or Casinghead Gasoline, and must be shipped in metal drums or barrels complying with Specification No. 5; or in ordinary tank cars, 60 lbs. test class, equipped with mechanical arrangement for closing of dome covers as specified in Master Car Builders' specifications for tank cars.

Every tank car containing liquid condensates, either blended or unblended, including liquefied petroleum gas, as defined herein, must have safety valves set to operate at 25 lbs. per sq. in. with a tolerance of 3 lbs. above or below, and the mechanical arrangements for closing the dome covers for such cars must either be such as to make it practically impossible to remove the dome cover while the interior of the car is subjected to pressure; or suitable vents that will be opened automatically by starting the operation of removing the dome cover must be provided.

The shipper must attach securely and conspicuously to the dome and dome cover three special white dome placards measuring 4 x 10 in., bearing the following wording:

10 Inches

4 Inches

CAUTION

AVOID ACCIDENTS

DO NOT REMOVE THIS DOME COVER WHILE GAS PRESSURE EXISTS IN TANK

Keep Lighted Lanterns Away

One placard must be attached to each side of the dome and one placard must be attached to the dome cover. The presence of these

special dome placards must be noted on the shipping order by the shipper and by the carrier on the billing accompanying the car. Placards must conform to samples furnished by the Chief Inspector of the Bureau of Explosives.

1825. (a) Packages containing inflammable liquids must not be entirely filled. Sufficient interior space must be left vacant to prevent leakage or distortion of containers, due to increase of temperature during transit. In all such packages this vacant space must not be less than 2 per cent of the total capacity of the container. In tank cars the vacant space must not be less than 2 per cent [38] of the total capacity of the tank, i.e., the shell and dome capacity, combined. If the dome of tank cars does not provide this 2 per cent, sufficient vacant space must be left in the shell of the tank to make up the difference.

Inflammable Placard.

1913. A placard of diamond shape, printed on strong, thin, white paper for pasting on tank cars and on strong tag board for tacking to wooden cars or to wooden boards of suitable size attached for this purpose to metal box cars or tank cars, measuring 10¾ in. on each side, and bearing in red and black letters the following inscription, must be securely attached to each outside end and to each side door of a box or stock car containing one or more packages protected by the *red* or the *yellow* diamond label, and to each side and end of a tank car containing an inflammable liquid (see p. 467).

Note—Cars containing cylinders of compressed non-inflammable gases (green label) do not require placards.

The method of making vapor-pressure tests is given in Chapter XVI, although this may soon be modified. For regulations on handling and unloading tank cars see B. E. Pamphlet No. 9.

The regulations of the Interstate Commerce Commission are now under discussion by all interested parties and the publications of the Commission, the American Petroleum Institute, and the Association of

[38] An outage of 2 per cent is frequently insufficient for light petroleum products, owing to the fact that they expand more than heavier petroleum products when the temperature increases, and this rate of expansion varies with the specific gravity of the material. It is recommended that when tank cars are loaded with gasoline or casinghead gasoline (see Par. 1824 [k]) the outage in tank shall not be less than the following:

Temperature of Product When Loaded	Minimum Outage Required When Gravity is		
	56-60° B.	60-70° B.	70-80° B.
	Per Cent	*Per Cent*	*Per Cent*
0 to 60° F.	3.2	3.5	4.1
61 70° F.	2.5	2.8	3.3
71 80° F.	2.0	2.1	2.4
81 100° F.	2.0	2.0	2.0

Natural Gasoline Manufacturers should be consulted in regard to revisions and changes.[39]

Explosions, such as that at Ardmore on Sept. 27, 1915, and that at Memphis on Jan. 24, 1921, in which serious loss of life and property occurred, have emphasized the importance of care in handling and transporting natural-gas gasoline, and have shown the necessity of intelligent regulation and standardized practice. Both of these explosions were caused by the removal of tank-car dome covers before the pressure in the car had been released.

Methods for handling these volatil and inflammable petroleum products are worthy of careful study, and regulations should be strictly enforced. The pressure within the tank-car should always be released before the dome-cover is removed. The Bureau of Explosives has approved the equipping of dome-covers with a two-inch nipple and stop-valve to which a line may be attached through which the gas and

[39] See "Hazards Involved in the Transportation Natural-Gas Gasoline," published jointly by the Bureau of Mines and the Association of Natural Gasoline Manufacturers, January, 1922. Also see the report of the Association of Natural Gasoline Manufacturers Committee in I. C. C. regulations, 1922.

vapor within the car can be piped to the refiner's compression or absorption plant. If such a connection cannot be made, the gas should be released by opening the safety valves with the ordinary tripod valve lifter, and a hooded arrangement provided that will fit over the valves as closely as possible. By applying suction a large part of the gas and vapor may thus be saved. When the pressure in the car is reduced to 1 pound the lines should be disconnected and the pressure reduced to zero before removing the dome-cover.

When the dome-cover is removed the contents of the car may be gaged by the use of a wooden pole. Measure the outage rather than the actual contents of the car. Do not use metal rods, for in warm weather these get hot and when placed in contact with the volatil distillate cause boiling and make accurate measurement impossible. The same precaution applies to the taking of samples. The container should be at least as cool as the liquid within the car.

The most desirable method of unloading natural gasoline is to allow it to flow by gravity to tanks underground or at a lower level. The use of compressed air introduces an unnecessary hazard. If a pump is used it should be located below the level of the car for otherwise, particularly in warm weather, the volatilization of the distillate and evolution of gas will break the pump-suction. A satisfactory scheme is to run an unloading line below ground along the entire length of the unloading-rack. Before opening the outlet valve of the car, naphtha should be circulated through the unloading line. In this manner the line and the pump are filled with liquid and difficulty is eliminated. Some refiners use a two-way suction-line and pull naphtha and the contents of the car through the pump together. Inasmuch as natural-gas gasoline, in order to avoid loss, should be blended as soon as it reaches the refinery, this procedure for avoiding pumping difficulty is justified. The mechanical mixing in the pump is an efficacious method of blending.

If the natural-gas gasoline is to be pumped to a blending tank, the discharge line from the pump should terminate in a manifold connection to several perforated pipes near the bottom of the storage tank. Better mixing is thus accomplished than if the gasoline is introduced in a single stream.

Rotary pumps are to be preferred to piston pumps for handling gasoline, but if piston pumps are used they will be found to work best if the clearance in the liquid end is reduced to a minimum. The liquid remaining in the cylinder at the end of the discharge stroke volatilizes in part in the interval between the discharge and suction stroke and during the early part of the suction stroke, and thus reduces the capacity of the pump. Pipe lines for handling natural-gas gasoline should be placed below ground as far as possible in order to keep them cool.

Natural-gas gasoline can be handled at the refinery with losses as low as 3 per cent from the time the cars are opened until the finished motor-gasoline is loaded. But general results are not so good as this

as is indicated by a tabulation given by W. P. Dykema [40] of losses in blending and shipping compression plant products in the Mid-Continent field.

	Loss Expressed as a Per Cent of Product Handled
Weathering	5-20
Transferring to loading station	2- 7
Loading in car tanks	1- 5
Shipping in standard cars	2-10
Total losses	10-42

California companies shipping raw condensate in trucks for distances of 2 to 40 miles report losses ranging from 2 to 7 per cent. Losses in pipe line shipments of 1 to 40 miles are reported as varying from 1 to 6 per cent. The insulated tank-car has demonstrated its superiority over the ordinary car, as users report a maximum loss of only 2½ per cent for long shipments in hot weather, and no loss during short hauls in rainy or cold weather.

Testing Natural Gas for Gasoline Content.

Two matters of fundamental importance that must be settled before a gasoline plant is built are: (1) Is there a sufficient supply of gas available, and is the supply certain to be maintained in paying quantity and quality in the future? (2) What is the chemical composition of the gas? If the answers to these questions are favorable the operator may proceed in confidence. Most of the failures in the natural-gas gasoline business can be attributed to insufficient study of gas supply and gas quality. The investigation should not stop with a study of the mixed gases from various sources, but should be followed to the individual well, or, at least, to the mixtures from small groups of wells.

The laboratory methods used to analyze coal-gas and similar gases are of little value in determining the composition of natural gases with which the analyst is not familiar. The numerous hydrocarbons of natural gas cannot be separated by the use of burette and various reagents in pipettes, nor can they be determined by explosion analysis. The results of an explosion or combustion analysis may be calculated in terms of methane and pentane or methane and hexane, and in this manner an empirical correlation can be developed between the results of analyses calculated in this way and those of suitable, but time-consuming, analytical methods. As routine methods for plant control, the combustion analysis, or the determination of specific gravity of the gas by the effusion method, will be found useful. Results by these methods must be carefully correlated with plant operation over a period of time before they are to be relied upon as a check on plant results. For details of the usual methods of gas analysis reference should be

[40] U. S. Bur. Min., *Bull. 151*, 93.

made to the standard work of Professor A. H. White or that of Professor L. M. Dennis.

The usual methods of gas analysis will be used, of course, to determine the oxygen content of casinghead gases and other gases collected under conditions that could result in air leakage. Occasionally natural gases contain carbon dioxide in such percentages as to make the determination of this component desirable.

The most desirable method of analysis would be one that would determine the actual percentages of the several hydrocarbons in natural gas. This is extremely difficult on account of the chemical similarity of these substances. The only resort is to a method that takes advantage of differences in the specific physical properties. Such a method is that of fractional distillation at low pressures as developed and used by Burrell, Seibert, and Robertson.[41] This procedure requires the services of an expert analyst, and also is exceedingly time consuming. It cannot be considered as a routine procedure.

It is now customary to test gas that is to be treated by the compression process with a portable equipment that is capable of handling small volumes of gas in the same way that the plant would or does handle large volumes. The apparatus can be conveniently mounted on a motor-truck, and so moved about as required, or can be hauled from place to place. An apparatus of the latter type is built by the Bessemer Gas Engine Company and described in the Bessemer Manual of Gasoline Recovery on pages 39 to 42. It is stated there that it is seldom advisable to make condensate of higher gravity than 90 to 92° Bé., and that, as a safety factor, an allowance for a 20 per cent loss should be made in using the results of the test in estimating plant performance.

Any apparatus of this nature should comprise a small pressure tank of 3 or 4 cu. ft. capacity, a two-stage compressor capable of compressing 5 or 6 ft. of free-gas per minute to a pressure of 250 lbs., a gas-engine that can drive the compressor, a cooling-coil consisting of 25 to 30 ft. of ¾-in. or 1-in. pipe immersed in a suitable tank, an accumulator tank, pressure gage, reducing valve and meter. The pressure of the gas is reduced nearly to that of the atmosphere before being passed through the meter. Provision must also be made to take the temperature of xiting gas. Also, a double coil may be used in which the comed gas from the accumulator tank is expanded, and the gas, on its om the pipe-coil to the accumulator, cooled.

uent source of error in portable compressor tests is the use rate meter. If an ordinary domestic meter is used it should y calibrated, and should not be used at pressures of more nches of water pressure. A manometer should be placed alongside the meter for the measurement of the pressure of the gas entering the meter. A small orifice meter is preferable, in my opinion, to any of the mechanical types for the measurement of small gas flows.

[41] U. S. Bur. Min., Tech. Paper 104, "Analysis of Natural Gas and Illuminating Gas by Fractional Distillation in a Vacuum at Low Temperatures and Pressures," 1915. U. S. Bur. Min., Tech. Paper 54, "Errors in Gas Analysis Due to the Assumption That the Molecular Volumes of all Gases are Alike," 1913.

Absorption Test.

According to Dykema and Neal[42] the only accurate method for determining the gasoline content of natural gas that contains less than 1 gallon of gasoline per 1,000 cu. ft. is the absorption test. In my opinion this test should also be used in analyzing "wet" gases, as a check on the compression test. A suitable apparatus is described by Dykema and Neal as follows:

"The apparatus shown in Figure 133 comprises a piece of 6-in. casing with five separate compartments, which can be connected in series. Each compartment has a ¾-in. gas inlet, and a 2-in. gas discharge pipe or chamber, which extends to a point near the bottom of the compartment. From an opening near the top of the compartment extends a ⅜-in. pipe coiled around a 3-in. core with seven turns, through which the gas being treated bubbles and in which most of the absorption takes place. A minor modification, optional in the design and not shown in the sketch, is the use of needle valves at each extremity of the apparatus in order that gas may not be introduced too rapidly, or may be throttled to any desired pressure so as not to carry oil over from one compartment to the next. Also, the use of a needle valve on the discharge end enables one to regulate more easily the rate of flow through the meter, especially in tests at low pressures—that is, when the gas flows through the absorber very slowly. It is advantageous to use gate valves instead of drain cocks for drawing off treated absorption oil from the oil chambers, as such valves facilitate rapid work and eliminate the possibility of volatilization losses that exists when oil is allowed to spray through a stopcock under pressure into the container for collecting treated oil. Also, time can be saved by using small bull-plugged nipples in place of standard plugs, as they can be more easily removed and more rigidly connected to prevent leaks.

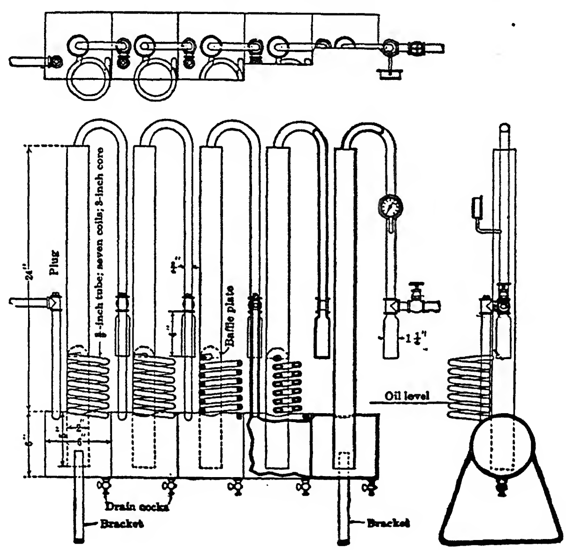


FIG. 133.—Absorption Tester.

[42] U. S. Bur. Min., Tech. Paper 232, 35.

Method of Using.

"To make the test with this absorber, 2,700 cc. of 'mineral seal oil,' or enough to bring the level of the oil, about 2 in. above the top of the 6-in. casing and well above the coil inlet, is accurately measured and introduced into each compartment. The most important requisite for absorption media is high initial boiling point, in order that in the subsequent distillation a quantitative separation can be effected. The oil used in the tests described in this paper had the following physical properties:

PROPERTIES OF OIL USED IN TESTS

Gravity	36.0° Bé.
Initial boiling point	450° F.
Viscosity	51 Saybolt
Flash point (Pensky-Martens closed tester)	271° F.
Fire test (Pensky-Martens open tester)	307° F.

"In most tests only the first three absorbers are used, but it may be expedient to fill the fourth compartment when examining rich gas flowing at low pressures or when running a large volume of dry gas in paralleling a 12-hour or day's operation of an absorption plant to determine the efficiency of recovery. The fifth compartment is not intended to be used as a container for oil, but to serve as a separator or oil trap in case any oil is carried over from the preceding compartment. A meter capable of accurately measuring 1 to 1,000 cu. ft. of gas is connected to the discharge of the absorber.

"The gas to be tested is allowed slowly to enter the apparatus with the discharge valve closed. When pressure equilibrium with the gas to be examined is obtained, or when the desired pressure is attained the discharge valve is opened enough to permit the desired rate of flow through the meter.

"The gas entering the absorber bubbles up through the oil, the latter absorbing the gasoline. The function of the pipe-coil is to provide a long and intimate contact between the oil and the gas as the gas passes through the absorber.

"After the desired quantity of gas has passed through the absorber the supply is shut off and the pressure is released, through the needle discharge valve, allowing all the gas to flow through the meter. After the pressure has decreased to atmospheric pressure the oil is withdrawn from each compartment and is accurately measured, 1,000 c.c. of treated oil from each compartment being kept for distillation.

Distillation of Saturated Oil.

"Of the treated oil 400 c.c. is introduced into a 500-c.c. Engler distilling flask connected to a condenser made of ½-in. brass tubing and surrounded with cold (ice) water contained in a metal box.[43]

[43] *Am. Soc. Test. Mat. Yr. Bk.*, 1915, 15, 568-569, and *Yr. Bk.*, 1916, 16, 518-521.

"The flask is heated by direct fire, slowly at first, and the gasoline driven out of the oil is collected in a graduated cylinder. The flask is heated until the vapor reaches a temperature of 350° F., which usually requires 20 minutes. If the oil has a very high saturation, it is allowed to cool 20 to 30° and again raised to 350°. This procedure is followed until practically no more gasoline is driven over and collected from the condenser.

"The recovery of gasoline will depend upon the rate of flow, gasoline content of the gas, volume of gas treated, pressure, and the temperature of the absorbing oil. Optimum conditions as regards volumes of gas and rate of flow with gases at different pressures and gasoline content are given below.

CONTROLLING FACTORS IN OPERATION OF TEST ABSORBER

Maximum Rates of Flow of Gas (Cubic Feet per Hour)	Pressure (Pounds per Square Inch)	Maximum Gas Capacity	
		Cubic Feet of Gas Treated	Gasoline Gallons per 1,000 Cubic Feet
400	300	800	0.125
200	150	400	.250
100	75	200	.50
50	40	150	.75
20	Atmospheric	100	1.00
		66	1.50
		50	2.00
		35	3.00
		25	4.00

"The following data were obtained from a representative test of intake gas at a compression plant in the Mid-Continent field.

RESULTS OF TEST OF INTAKE GAS AT A COMPRESSION PLANT

Temperature of oil,	94° F.
Pressure of gas treated,	204 lbs. per sq. in.
Rate of flow,	133 cu. ft. per hour.
Volume of gas treated,	302 cubic feet.

Item		Compartments		
		First	Second	Third
Charge	c.c.	2,600	2,600	2,600
Quantity recovered	c.c.	2,700	2,600	2,630
Gravity of oil	° B.	37.0	36.4	36.0
Quantity distilled	c.c.	400	400	400
Initial boiling point	° F.	170	185	308
Gasoline in 400-c.c. sample	c.c.	19.5	9.5	3.5
Gasoline recovered in each compartment.	c.c.	131.5	63.2	23
Proportion recovered in each compartment	per cent	60.5	29.0	10.5

"Total quantity of gasoline recovered, 217.7 cubic centimeters (gravity, 78° Bé.). Gasoline content of gas treated, 0.190 gallon per 1,000 cubic feet. The gasoline content is calculated by using the following formula:

$$Q = \frac{1000}{G} \times \frac{C}{3785}$$

where Q is the gasoline content in gallons per 1,000 cu. ft. of gas, G is the volume in cubic feet of gas treated, and C is the total number of cubic centimeters of gasoline obtained from the treated absorption medium.

"Above certain limits the temperature of the absorbing oil has prob-

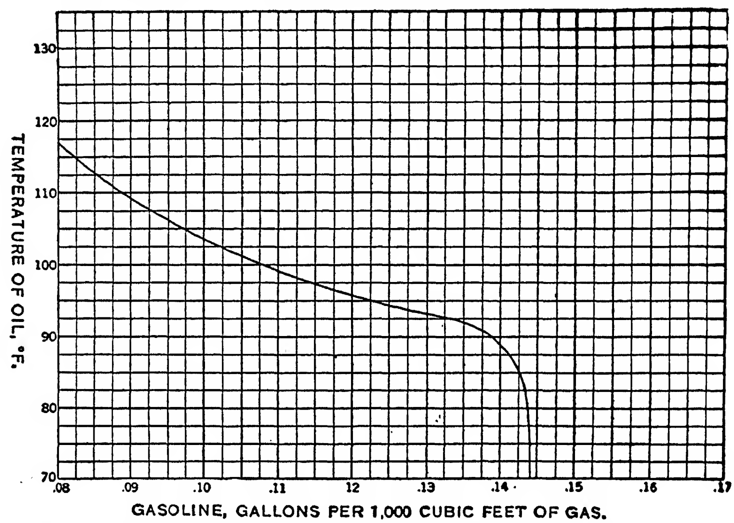


FIG. 134.—Curve Showing Effect of Temperature on Absorption.

ably more effect on the efficiency of recovery than any other factor. In a series of tests of "dry" natural gas with all conditions constant, except the variable factor of temperature, a difference of 42 per cent in the volumetric recovery of gasoline for a gradient of 30° F. was obtained, as is shown by the curve in Figure 134. These changes took place between 90° F. and 120° F., and are undoubtedly due to the rapid increase in the partial vapor pressure of the gasoline fractions in the gas as the boiling points are reached. Probably no two gases will show the same results with the same variation in temperature, inasmuch as the characteristics of the gasoline hydrocarbons are distinctly dissimilar.

"The data from which this curve was plotted were obtained from a series of tests using a constant quantity of oil (2,600 c.c. in each of the first three compartments), a pressure of 130 lbs. per sq. in., and a total volume of 200 cu. ft. of gas which passed through the apparatus

at the rate of 2 cu. ft. per minute. The point should be emphasized that the data obtained in this test cannot be taken as a criterion by which to judge other natural gas. Samples of natural gas from different wells may have the same gasoline content, but on account of differences in the characteristics of the various hydrocarbons present may require radically different treatment.

"The test absorber and the method described in this paper are recommended in preference to the use of the scrubbers mentioned in other publications, because they give more significant results when evaluating a gas with the idea of determining the feasibility of installing an absorption plant, or ascertaining the efficiency of recovery at absorption or compression plants."

Charcoal Absorption Method.

The analytical method in which charcoal is used as an adsorbent is open to a number of objections. It is described by R. P. Anderson and C. E. Hinchley,[44] in Day's Handbook,[45] by Hamor and Padgett,[46] and by Oberfell, Shinkle, and Meserve.[47] The method can be adapted for control purposes, but, on account of the cut and dried procedure required when a new gas is to be analyzed, it can scarcely be regarded as suitable for general use.

The Patent Situation in the Natural-gas Gasoline Industry.

Like most other new and developing industries the natural-gas gasoline industry has its patent problems. These are of a more urgent nature at present in the manufacture of gasoline by the absorption process than by the compression method. The company that sells by far the largest part of the equipment for the compression plants licenses each operator under U. S. Patent 933,976 issued to John L. Gray, September 14, 1909. But the absorption plant operator cannot be entirely sure of his ground until the litigation of the Saybolt patent is concluded.

In March, 1917, the Standard Oil Company of New Jersey and the Hope Natural Gas Company brought suit in equity against the Oklahoma Natural Gas Company for infringement of the Saybolt patent. This U. S. patent, numbered 987,927, dated April 18, 1921, and entitled "Obtaining Naphtha from Natural Gas," was issued to George M. Saybolt, and assigned by him to the Standard Oil Company of New Jersey. This corporation, on January 22, 1916, made formal grant (conforming with an earlier arrangement) of an exclusive license to the Hope Natural Gas Company. The licensee was thereby permitted to operate under the Saybolt patent, and to license others so to do.

On April 22, 1919, the case was argued before Judge R. L. Williams of the Federal Court of the Eastern District of Oklahoma at Muskogee. The testimony of both sides, including exhibits, covered 1500 printed pages, the attorney's briefs 500, and a "Fac Simile of Book

[44] *J. Ind. Eng. Chem.*, 12 (1920), 735-8.
[45] "Handbook of the Petroleum Industry," I, 763-4.
[46] "The Examination of Petroleum," 273-6.
[47] *J. Ind. Eng. Chem.*, 11 (1919), 197-200.

References Showing Old and Wide Dissemination of Henry's Law of Absorption of Gasoline" 200 more, or in all about 2,200 pages. In July, 1921, Judge Williams declared the Saybolt patent invalid, and dismissed the complainant's bill.

On August 1, 1921, the complainants filed an appeal in the Federal Court of Appeals, and the case was set for a hearing May 17, 1922, at St. Paul, Minnesota. On October 3, 1922, the decision of Judge Williams was upheld by the U. S. Circuit Court of Appeals at St. Louis in an opinion rendered by Judge Carland.

While Judge Carland's decision has done much to clear the air, the situation is still one to be carefully considered by anyone wishing to manufacture gasoline by the absorption process. Appeal may yet be taken to the U. S. Supreme Court. The Hope Natural Gas Company's contract calls for payment of a royalty of 10 per cent on the first 10 cents of the price at which the gasoline is sold, and 20 per cent of current market price above 10 cents per gallon. Several adjunct and supporting patents issued to H. C. Cooper and J. B. Garner, and others pending may have some bearing on the situation as a whole.

Statistics.

The statistical tables that follow will be found of interest:

TABLE LXVI

NATURAL-GAS GASOLINE PRODUCED IN THE UNITED STATES[48]

Year	Number of Operators	Number of Plants	Gasoline Produced			Gas Used (Estimated)		
			Quantity (Gallons)	Value	Average Price in Cents per Gallon	Volume M. Cu. Ft.	Value [a]	Average Yield of Gasoline per M. Cu. Ft. (Gallons)
1911 ...	132	176	7,425,839	$531,704	7.2	2,475,697	$176,961	3.0
1912 ...	186	250	12,081,179	1,157,476	9.6	4,687,796	331,985	2.6
1913 ...	232	341	24,060,817	2,458,443	10.2	9,889,441	566,224	2.4
1914 ...	254	386	42,652,632	3,105,909	7.3	16,894,557	889,906	2.4
1915 ...	287	414	65,364,665	5,150,823	7.9	24,064,391	1,202,555	2.6
1916 ...	460	596	103,492,689	14,331,148	13.8	208,705,023	14,609,300	0.50
1917 ...	750	886	217,884,104	40,188,956	18.4	429,287,797	34,343,000	0.51
1918 ...	[b]503	1,004	282,535,550	50,363,535	17.8	449,108,661	40,419,700	0.63
1919 ...	[b]611	1,191	351,535,026	64,196,763	18.3	480,403,963	41,314,700	0.73
1920 ...	[b]576	1,154	384,743,922	71,788,122	18.7	496,430,952	41,700,000	0.78
1921[c] ...	....	1,161	473,658,500	65,717,900	14.0	469,426,600	....	1.0

[a] The value of the gas is based on sales to gasoline producers, not on sales for domestic or industrial purposes.

[b] The figures for the number of operators in 1918, 1919, and 1920 are not comparable with those for earlier years, as the method of listing has been changed.

[c] Preliminary estimate of U. S. Geol. Survey.

TABLE LXVII

PERCENTAGE OF NATURAL-GAS GASOLINE PRODUCED BY EACH STATE—1911-1920[49]

State	1911	1912	1913	1914	1915	1916	1917	1918	1919	1920
Ohio	23	14	9	6	3	3	3	2	3	3
Oklahoma	5	13	27	40	48	47	53	58	54	46
Pennsylvania ..	20	17	15	11	9	9	6	6	6	5
West Virginia .	49	44	32	21	17	18	15	13	15	15
California		9	14	18	20	17	13	11	11	13
Illinois				3	2	2	2	2	2	2
Kentucky	3	3				1	1	1	1	1
New York			3	1					[a]1	[a]1
Colorado					1	1		1	....	....
Kansas	......	......					2		([a])	([a])
Louisiana	......	......	......	......		1	3	2	3	3
Texas	......	......	......	......		1	2	3	3	9
Wyoming	......	......	......	......	......	......	......	1	1	2
	100	100	100	100	100	100	100	100	100	100

[a] New York and Kansas together, 1 per cent.

[48] From "Natural-Gas Gasoline in 1917," "Natural-Gas Gasoline in 1920." Both separates from "Mineral Resources" by the U. S. Geological Survey.

[49] "Natural-Gas Gasoline in 1920," U. S. Geological Survey.

TABLE LXVIII

DETAILS OF NATURAL-GAS GASOLINE INDUSTRY IN 1920 BY STATES [60]

State	Number of Operators	Number of Plants	Gasoline Produced: Quantity (Gallons)	Gasoline Produced: Value	Gasoline Produced: Average Price per Gallon (Cents)	Gas Used: Estimated Volume (M. Cubic Feet)	Gas Used: Average Yield per M. Cubic Feet (Gallons)	Percentage of Total Production: State: Compression	State: Absorption	United States: Compression	United States: Absorption	United States: Total
Oklahoma	141	315	178,856,929	$31,334,493	17.5	85,167,518	2.10	92	8	58.3	14.4	46.5
West Virginia	74	211	58,941,488	13,049,551	22.1	174,320,058	.34	27	73	5.7	41.5	15.3
California	30	70	48,207,976	8,323,819	17.3	43,772,395	1.10	73	27	12.6	12.4	12.5
Texas	20	42	32,956,028	5,770,809	17.5	15,852,213	2.08	91	9	10.7	2.7	8.6
Pennsylvania	207	306	21,151,135	4,382,380	20.7	60,951,697	.35	52	48	3.9	9.8	5.5
Louisiana	14	31	10,609,629	1,712,613	16.1	37,754,043	.28	57	43	2.2	4.4	2.7
Ohio	31	59	10,015,638	2,194,558	21.9	40,215,329	.25	23	77	.8	7.4	2.6
Wyoming	4	5	8,711,037	1,735,828	19.9	4,809,277	1.81	94	6	2.9	.5	2.3
Illinois	38	92	6,054,916	1,307,980	21.6	2,889,334	2.10	100	......	2.1	......	1.6
Kentucky	6	9	4,497,320	1,071,628	23.8	18,939,285	.24	4	96	.1	4.2	1.2
Kansas	8	10	4,330,748	828,887	19.1	11,597,340	.37	36	64	.6	2.7	1.1
New York	4	4	411,078	75,576	18.4	162,463	2.53	100	......	.1	......	.1
Total, 1920	[a]576	1,154	384,743,922	71,788,122	18.7	496,430,952	.78	73.1	26.9	100.0	100.0	100.0
Total, 1919	[a]611	1,191	351,535,026	64,196,763	18.3	480,403,963	.73	74.3	25.7	100.0	100.0	100.0

[a] The figures for the number of operators in 1918, 1919, and 1920 are not comparable with those for years prior to 1918, as the method of listing has been changed. See footnote [a], p. 296, "Natural-Gas Gasoline in 1920."

[60] "Natural-Gas Gasoline in 1920," U. S. Geol. Sur.

TABLE LXIX

Natural-Gas Gasoline Produced in the United States in 1920, by Principal Methods of Manufacture

PRODUCED BY COMPRESSION AND BY VACUUM PUMPS

State	Number of Plants	Gasoline Produced: Quantity (Gallons)	Gasoline Produced: Value	Gas Used: Average Price per Gallon (Cents)	Gas Used: Estimated Volume (M. Cubic Feet)	Gas Used: Average Yield per M. Cubic Feet (Gallons)
Oklahoma [a]	268	163,913,791	$28,433,105	17.3	48,671,472	3.37
California [b]	44	35,347,691	6,619,893	18.7	27,856,279	1.27
Texas	35	30,144,880	5,272,276	17.5	10,098,420	2.99
West Virginia [c].	163	15,972,833	3,169,859	19.8	11,605,174	1.38
Pennsylvania ...	279	10,981,461	2,128,774	19.4	5,391,467	2.04
Wyoming	4	8,175,825	1,609,762	19.7	2,345,048	3.49
Louisiana	18	6,077,093	831,086	13.7	1,917,159	3.17
Illinois	92	6,054,916	1,307,980	21.6	2,889,334	2.10
Ohio	47	2,294,996	466,747	20.3	916,075	2.51
Kansas	7	1,574,482	315,906	20.1	780,820	2.02
New York	4	411,078	75,576	18.4	162,463	2.53
Kentucky	6	182,927	41,997	23.0	254,091	.72
	967	281,131,973	50,272,961	17.9	112,887,802	2.49
Total, 1919 ...	1,025	261,157,587	45,563,458	17.4	117,669,332	2.22

PRODUCED BY ABSORPTION [d]

State	Number of Plants	Quantity (Gallons)	Value	Average Price per Gallon (Cents)	Estimated Volume (M. Cubic Feet)	Average Yield per M. Cubic Feet (Gallons)
West Virginia [e].	48	42,968,655	$9,879,692	23.0	162,714,884	0.26
Oklahoma [a]	47	14,943,138	2,901,388	19.4	36,496,046	.41
California [f]	26	12,860,285	1,703,926	13.2	15,916,116	.81
Pennsylvania ...	27	10,169,674	2,253,606	22.2	55,560,230	.18
Ohio	12	7,720,642	1,727,811	22.4	39,299,254	.20
Louisiana [g]	13	4,532,536	881,527	19.4	35,836,884	.13
Kentucky	3	4,314,393	1,029,631	23.9	18,685,194	.23
Texas	7	2,811,148	498,533	17.7	5,753,793	.49
Kansas	3	2,756,266	512,981	18.6	10,816,520	.25
Wyoming	1	535,212	126,066	23.6	2,464,229	.22
	187	103,611,949	21,515,161	20.8	383,543,150 [h]	.27
Total, 1919 ...	166	90,377,439	18,633,305	20.6	374,928,966	.24

[a] Includes two combination compression and absorption plants.
[b] Includes three combination compression and absorption plants.
[c] Includes six combination compression and absorption plants.
[d] Includes drip gasoline.
[e] Includes five combination compression and absorption plants.
[f] Includes seven combination compression and absorption plants.
[g] Includes four combination compression and absorption plants.
[h] Includes 12,194,335 M. cubic feet of gas that was first treated at combination plants by compression and that is included in the total volume of gas treated at the compression plants but not duplicated in the total for the United States.

SELECTED AND ADDITIONAL REFERENCES

Although numerous references have been given in the context of this chapter the list that follows will be found useful. Some of the titles have already been given and are repeated here because of the importance of the work referred to. Several of the bulletins and more comprehensive reference works will be found to contain citations of numerous further sources of information on the history and technology of the natural-gas gasoline industry.

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Chapter XII.

Alcohol.

A Motor Fuel of the Future.

The present importance of alcohol as a motor fuel can scarcely justify the inclusion in this book of even the very limited discussion given in the paragraphs that follow. The only fuel containing alcohol that has been or is now marketed in this country in quantity sufficient to merit comment is "Alcogas," a blended fuel made by the U. S. Industrial Alcohol Company. Alcohol, as such, is not used as a motor fuel at the present time.

The future development of the alcohol industry may easily extend beyond the bounds of the imagination of those most sanguine, not because growth will be easily accomplished, but because an insistent demand for motor fuel at good prices will provide the incentive for overcoming obstacles. Who can predict when this growth will come? It may be ten years, it may be twenty, but it is significant that it has already been started by a corporation some of whose substantial stockholders are not without exact knowledge of the petroleum industry.

Much impractical nonsense has been written about alcohol, such, for example, as statements to the effect that the denatured alcohol law would make every farmer a manufacturer of industrial alcohol from apple-parings, corn-cobs, or other by-products of the activities of the farm. Alcohol produced in this way today would possibly require a new definition of "industrial" in Webster. Argument of this nature is not likely to be used as political capital again, for were the farmer subjected, as a result of existent legislation, to the exasperations of the current supervision of alcohol plants there would speedily be a new group of office holders in Washington. I shall speak presently of the legal phase of alcohol production. My purpose in the following paragraphs is to present a brief summary of the possibilities of future alcohol production, and to include such other matter as demands comment. I recognize full well that a complete discussion of the present and future alcohol industry would require an entire volume, and I therefore include references to more complete sources of information.

Alcohol as a Motor Fuel.

Ethyl alcohol, as such, is not a satisfactory fuel for use in motors designed to use gasoline. On account of the fact that the vapor pres-

sure of ethyl alcohol is only about 1/4 that of gasoline at ordinary temperatures, and the latent heat of vaporization is about 3.2 times that of gasoline, difficulty is encountered in starting the engine. Air bubbled through alcohol at ordinary temperatures does not form explosive mixtures, whereas if bubbled through gasoline, mixtures too rich to explode can be formed. Difficult starting can be overcome by addition of ether to the alcohol, by priming the cylinders, or by the use of a special fuel for starting.

But there are further inherent difficulties. The net heat of combustion of alcohol is only 10,800 B.t.u. per pound as compared to about 19,000 for gasoline. However, alcohol can be burned under two or three times the maximum pressure under which gasoline can be used with avoidance of the fuel-knock. The greater efficiency resulting from the increased compression almost makes up for the lower available energy of the alcohol. It can therefore be said that if automobiles were equipped with engines suitable for handling air-alcohol mixtures the use of alcohol-ether fuel mixtures would be possible. For the present the use of such mixtures is precluded. Cars are not equipped with engines designed to burn alcohol, and they will not be so equipped until the owner of an alcohol-burning car will not be handicapped because of lack of distributive facilities for alcohol. The large investment required to maintain such facilities makes it improbable that they will soon be available. The obvious conclusion is that if alcohol is to be of importance as a fuel it will be as a component of a mixed fuel that can be used in engines and carburetor equipment of the type currently in use. Blended fuels will in all probability be distributed through the same channels as gasoline, as this will involve the minimum additional investment in facilities for conducting business. A recent contract of this nature between a large alcohol producer and a large gasoline marketing organization is a straw that shows the direction of the wind.

The acidic or aldehydic characteristics of the products of combustion of alcohol are sometimes cited as an objection to the use of this substance as a fuel. I am somewhat skeptical of the real seriousness of this difficulty, and doubt if it exists at all when composite fuels containing 35 to 40 per cent of alcohol are burned. M. J. P. Foster [1] states that 0.14 per cent by weight of ammonia is required to neutralize the corrosive gases formed when a fuel containing 55.5 per cent alcohol, 42.8 per cent ether, 1.1 per cent kerosene, and 0.56 per cent pyridine is burned. The pyridine forms 0.155 per cent NH_3 ammonia, which is more than enough to avoid the difficulty.

A point in alcohol's favor that should not be forgotten is its clean combustion. Carbon formation is nil. Not only alcohol, but mixtures containing 35 to 40 per cent of alcohol burn with practically negligible formation of carbon.

Alcohol is safer to handle and transport than gasoline because of its lesser volatility, and because it is miscible with water. A gasoline

[1] *Sugar*, June 20, 1920, 337.

fire is spread by the use of water in any attempt to extinguish it, but alcohol fires are readily extinguished with water.

It is not my purpose to discuss the utilization of fuels in this volume. The reader is referred to several [2] sources of information on the use of alcohol.

Alcohol and the Law.

The properties of ethyl alcohol are such that only a few of the many who have made its acquaintance have evinced any special interest in its industrial uses and importance. This applies not only to those who have found in alcohol a social lubricant, but also to those who believe that society is sufficiently convivial when its bearings run in water. In fact the lack of appreciation of the industrial importance of alcohol has threatened several times to make it impossible or very difficult for manufacturers and individuals to obtain alcohol for use in any of the thousand and one essential ways. Alcohol is a substance comparable to sulfuric acid in its fundamental industrial importance, and widespread use. It is unfortunate that this is not appreciated by the public.

The insistent desire of a large proportion of the citizens of this and other countries to avail themselves of the "lubricating" properties of alcohol led to the taxing of the commodity. In 1791 a tax was levied on distilled liquors, but Thomas Jefferson engineered the repeal of this law in 1802. The expense incident to the war of 1812 again led to the levying of a tax on spirits in 1813, but this law was repealed in 1817. No tax was then in force until the expense of the Civil War brought about the imposition of a tax of 20 cents per gallon. This was increased to 50 cents in 1868, to 70 cents in 1872, to 90 cents in 1875, to $1.10 in 1894. This rate continued in force until 1917 when it was increased to $3.20 per proof gallon for beverage spirits, and to $2.20 for non-beverage spirits. Thus 95 per cent ethyl alcohol for use in legitimate manufacturing enterprises was taxed at the rate of $\frac{95}{50} \times \$2.20 = \$4.18$ per gallon. A 40-cent commodity selling for over $4.00! It is difficult indeed to conjure up any reason why alcohol for manufacturing purposes should be taxed at all, let alone to the extent of 1000 per cent.

In 1906 the Denatured Alcohol Act was passed. This provided that ethyl alcohol could be mixed with methyl alcohol, or various other

[2] Judge, "High Speed Internal Combustion Engines." Pub. I. Pitman & Sons, 1918. Strong, R. M., Stone, L., "Comparative Fuel Values of Gasoline and Denatured Alcohol in Internal Combustion Engines." U. S. Bur. Min., *Bull. 43*, 1st Ed. 1912. Rep. 1918. Dixon, H. B., "Researches on Alcohol as a Fuel for Internal Combustion Engines." *Auto. Ind.*, Feb. 3, 1921, 211-15. Strong, R. M., "Commercial Deductions from Comparisons of Gasoline and Alcohol Tests on Internal-Combustion Engines." U. S. Geol. Sur., *Bull. 392*, 1909. Anon., *J. Soc. Auto. Eng.*, 5 (1919), 207. Scarratt, A. W., "The Carburetion of Alcohol," *J. Soc. Auto. Eng.*, 8 (1921), 328-30.

denaturants, and was then not taxed. The Commissioner of Internal Revenue under approval of the Secretary of the Treasury was made sponsor for carrying out the provisions of the act. This law has had a beneficial effect, though the red-tape has handicapped both user and manufacturer, and increased the cost of production of alcohol. If all laws were enforced with the fervor that animates those charged with the enforcement of revenue acts, this country might become a safe place in which all might enjoy those inalienable rights to life, liberty, and the pursuit of happiness.

It is to be hoped that the agitation leading up to and resulting in the passage of the National Prohibition Act has not so warped public opinion that the broad usefulness of alcohol will be unseen and forgotten in the darkness of its supposed iniquity. The development of the industry is handicapped, and the broad use of alcohol as a motor fuel endangered, by misinformation and by ignorant or fanatic over-enthusiasm in the enforcement of the Prohibition Act.

The National Prohibition Act purports to be: "An Act to prohibit intoxicating beverages, and to regulate the manufacture, production, use, and sale of high-proof spirits for other than beverage purposes and *to insure an ample supply of alcohol and promote its use in scientific research, and in the development of fuel, dye, and other lawful industries.*" The act comprised three principal titles, I. A provision for enforcement, II. Prohibition of Intoxicating Beverages, III. Industrial Alcohol. Title I. was automatically replaced by Title II. on Jan. 16, 1920, when the 18th Amendment came into effect.

The prohibition section of the law provides that it is unlawful to advertise, manufacture, sell, or possess for sale, any utensil, contrivance, machine, preparation, compound, tablet, substance, formula, direction or recipe, advertised, designed, or intended for use in the manufacture of alcohol, or it is unlawful to solicit or receive, or knowingly permit an employee to solicit or receive from any person an order for alcohol, or give any information as to how alcohol may be obtained, subject to certain exceptions.

On the other hand in the Industrial Alcohol Title, Section 13, it is provided, "That the Commissioner shall from time to time issue regulations respecting the establishment, bonding, and operation of industrial alcohol plants, denaturing plants, and bonded warehouses authorized herein, and the distribution, sale, export, and use of alcohol which may be necessary, advisable, or proper to secure the revenue, to prevent diversion of the alcohol to illegal uses, and to place the non-beverage alcohol industry and other industries using such alcohol as a chemical raw material, or for other lawful purpose, upon the highest possible plane of scientific and commercial efficiency consistent with the interests of the Government, and which shall insure an ample supply of such alcohol and promote its use in scientific research and the development of fuels, dyes, and other lawful products. All regulations so issued shall have the force and effect of law."

As is pointed out by Dr. M. C. Whitaker,[3] who of all men in this country is probably most familiar with the actual practical effect of the alcohol law and its enforcement, on the manufacture of industrial alcohol, "Under one section of the law you are forbidden to whisper the terrible word, because of its booze associations, while under another section you are required to proclaim alcohol from the housetops as a national necessity. In the administration of this law, when there is an apparent conflict of language, the prohibition officers appear to work under the injunction usually given to beginners learning to drive an automobile: 'When in doubt, push both feet.' Prohibition is regarded by them as their first duty, and when in doubt, stop everything—engine and all."

The ignorance of some of the agents to whom is entrusted the enforcement of the prohibition law, or the ridiculous interpretations of the law as written, is illustrated by several examples cited by Dr. Whitaker. These are too lengthy to be repeated here, but include such incidents as the following:

1. The general counsels of the telephone companies of Boston and Baltimore advised their clients that it would be illegal to list the name "U. S. Industrial Alcohol Company" in the phone book.

2. The U. S. Industrial Alcohol Company was advised by the Prohibition Commissioner that it would be illegal to use the words "Cologne Spirits and Alcohol, Pure and Denatured" on their letterhead.

3. E. B. Badger and Sons of Boston, manufacturers of distillation equipment, were advised by a clerk in a local bookstore that it would be illegal to sell them a copy of Young's "Fractional Distillation."

4. The agents of a steamship line at Baltimore refused to receive an export shipment of isobutyl alcohol. It was necessary to relabel the drums iso-butyl solvent, which camouflage was explained to the purchaser abroad with some difficulty.

After expending much time and effort these and other similar difficulties were usually adjusted. The danger does not lie so much in passing difficulties of this nature, but they are illustrative of the state of mind of those who are supposed to know enough to enforce the law intelligently. If some among these are so ignorant, what can be expected of the public at large, which, because of its almost entire unfamiliarity with the necessary uses and the tremendous future possibilities of alcohol, may be led to pass unwise and extreme measures by the sentimentality of some proponents of prohibition, by the misguided though sincere utterances from some pulpits, and by the fanatic speeches of some of those who guide the activities of such organizations as the Anti-saloon League.

I do not wish to be misunderstood. I am not presenting a brief for the saloon and liquor interests. A chemical engineer, or chemist, among all men, should be glad to see strong drink go, for he should be aware that alcohol is not a stimulant, as is popularly supposed, but is

[3] *J. Ind. Eng. Chem.*, 13 (1921), 647-50. The reader should refer to this article for important information on this general subject.

a depressant to be classed with the narcotic drugs. The merits of prohibition can be decided for the technical man without sentimentality.

But, though I may favor prohibition, my sense of fairness is aroused by the utterances of such men as Mr. C. R. O'Connor, for a time Federal Prohibition Director of New York, who is reported to have said, in answer to a protest by manufacturers regarding the reluctance of his office to approve permits to secure alcohol for use in their legitimate industrial operations, "Industrial alcohol be damned; you know it's all booze."

Mr. Wayne B. Wheeler, general counsel of the Anti-Saloon League, stated before the Judiciary Committee on May 20, 1921, "If it comes to a point where it must be a choice between medicaments for medical preparations and the enforcement of the law, I think we must choose law enforcement." Dr. Whitaker quite rightly brands this "do-or-die fanaticism."

Had it not been for the then Commissioner of Internal Revenue, Daniel C. Roper, the prohibition act would not have contained Title III relative to industrial alcohol. The bill for enforcement of the Eighteenth Amendment as presented to the Judiciary Committee by Mr. Wheeler, consisted only of Titles I and II. Such prejudice and ignorance or both is frequently typical of the leadership of reform movements, and makes thinking men slow to approve social experiments much of the impulse of which is sentimental or emotional. The need for education is clear, in order that public opinion shall be molded on a basis of fact.

Alcohol Production in the United States.

Detailed statistics of the production of alcohol in the United States are to be found in the annual reports of the Commissioner of Internal Revenue. The essential figures are presented in Tables LXX and LXXI.

TABLE LXX

PRODUCTION OF DENATURED ALCOHOL IN THE UNITED STATES

(Quantities are given in U. S. Gallons)

Fiscal Years *	Denaturing Warehouses	Completely Denatured	Specially Denatured	Total
1907	8	1,397,861	382,415	1,780,276
1908	12	1,812,122	1,509,329	3,321,451
1909	12	2,370,839	2,185,579	4,556,418
1910	12	3,076,924	3,002,102	6,079,027
1911	14	3,374,019	3,507,109	6,881,129
1912	14	4,161,268	3,933,246	8,094,515
1913	21	5,233,240	4,608,417	9,831,658
1914	25	5,213,129	5,191,846	10,404,975
1915	23	5,386,646	8,599,821	13,976,468
1916	33	7,871,952	38,807,153	46,679,106
1917	44	10,508,919	45,170,678	55,679,597
1918	49	10,328,454	39,834,561	50,163,016
1919	45	9,976,721	28,294,219	38,270,940
1920	52	13,528,402	15,307,947	27,836,350

* Fiscal years end June 30th.

Steady growth is shown from 1907 to 1916 when the war demands caused a tremendous but temporary increase.

TABLE LXXI

Production of Taxable Alcohol in the United States

Fiscal Years Ending June 30th	Production U. S. Gallons of 95% Alcohol
1910	82,100,000
1915	69,600,000
1916	131,000,000
1917	146,000,000
1918	91,400,000
1919	52,100,000
1920	52,500,000

The largest quantity of 95 per cent alcohol produced in this country was 202,000,000 gallons in 1917. The total production in the years ending June 30, 1920, was 81,000,000 gallons. Nearly all of the 1920 alcohol was made from molasses. The Commissioner reports that 1,374,428 bushels of grains were used in 1920, and 132,460,019 gallons of molasses. Louisiana leads in alcohol production, Illinois is second, and Maryland third.

The 202,000,000 gallons of alcohol produced in 1917 is not quite 4.5 per cent of the gasoline consumed in this country in 1921. The 1920 production of alcohol is only 1.8 per cent of the 1921 gasoline consumption. These figures serve to give one the necessary perspective for a discussion of alcohol as a motor fuel. The present production of alcohol is a drop in the bucket, sufficient, it is true, to make a very good business for a few corporations, but as the source of important quantities of motor fuel it is scarcely worthy of mention.

Can alcohol be produced in quantities sufficient to supply 10, 15, 20, or 30 per cent of this country's present motor-fuel requirements? This is the real question. The answer lies in a consideration of the availability of raw materials from which alcohol can be made. Technology is a small factor, except in the production of alcohol from wood. Here there is a real opportunity for chemical engineering development.

...minology in the Alcohol Industry.

...eader of the literature on alcohol, who is unfamiliar with its ...guage, may err through a misunderstanding of terms. It is high time that the industry and the Revenue Department discard the verbiage of the booze business and start to talk language that is definite ... by all. Let gallons be U. S. gallons, and not "proof" ...nd let strength be expressed in per cent by volume ...s so much "over-proof." Let the manufacturing ...lled "plants" and not "distilleries." The effect ...ry. However, terms appear in the literature and

U. S. Proof Spirit[4] is a mixture of ethyl alcohol and water that contains 50 per cent by volume of alcohol of a specific gravity of 0.7939 at 60° F. referred to the maximum density of water as unity. Hence, twice the volume percentage of alcohol in any mixture with water gives the proof. Thus 95 per cent alcohol by volume is 190 proof.

The U. S. Wine gallon is the same as the U. S. Standard gallon of 231 cu. in.

The U. S. Taxable gallon is the proof gallon, or the wine gallon when the spirit is under proof.

The barrel referred to in writings on the alcohol industry is one of 50 gallons, each of 231 cu. in., in place of the 42 gallon barrel of the petroleum industry.

British proof spirit is defined by law as spirit that at 51° F. weighs $\frac{12}{13}$ as much as distilled water. The temperature of the water is not given. Presumably it is assumed to be 51° F. The specific gravity of British proof spirit at $\frac{51^\circ \text{ F.}}{51^\circ \text{ F.}}$ is 0.92308, and at $\frac{60^\circ \text{ F.}}{60^\circ \text{ F.}}$ 0.91976. It contains 49.28 per cent alcohol by weight or 57.1 per cent by volume. It should also be recalled that the British gallon is 277.418 cu. in., or 1.20094 U. S. gallons.

In the United States, Great Britain, and France it is customary to talk about the strength of alcohol in terms of per cent by volume. In Germany strength is expressed in per cent by weight.

The Production of Alcohol by Fermentation.

The alcohol of commerce is nearly all produced by the fermentation of sugars with the aid of the enzymes of yeast. The sugar may be present in the raw material, as when molasses or beet juice is used, or it may be formed by hydrolysis, as when starchy or cellulosic materials are used. It is out of the question for me to attempt to go into the subject of alcoholic fermentation in detail. The larger works on alcohol and on fermentation must be consulted by the reader.

Enzymes are nitrogenous substances of high molecular weight that act as specific catalysts. The amylolytic or diastatic enzymes catalyze the hydrolysis of starches, the lipolytic the hydrolysis of fats, and the proteolytic the hydrolysis of proteins. Invertase and maltase hydrolyze sucrose and maltose respectively. Among the oxidases, zymase, the enzyme that aids the conversion of the hexose sugars glucose and fructose into alcohol and carbon dioxide, is the most important.

Enzymes in general are colloid substances. When dry they may be heated to temperatures of 100 to 125° C. without destroying their catalytic properties, but in aqueous solutions temperatures of 80 to 90° C. only are required to destroy their activity. The enzymes, as might be

[4] Revised Statutes, Sec. 3249.

expected, function to best advantage at temperatures near those of their normal environment. Temperatures between 25 and 30° C. are those used in the manufacture of alcohol. The reactions of fermentation are oxidations, and evolve heat. For this reason cooling means must be provided in fermenting tanks in order that the desired temperature can be maintained.

The most unfortunate thing about fermentation is the waste of almost one-half of the raw material through conversion into carbon dioxide. The equation representing the alcoholic fermentation of a hexose sugar may be written.

$$\underset{180}{C_6H_{12}O_6} \xrightarrow{\text{Fermentation}} \underset{92}{2C_2H_5OH} + \underset{88}{2CO_2}$$

The theoretical yield from a hexose sugar is 51.1 per cent, from cane sugar or maltose 53.8 per cent, and from starch 56.8 per cent. The yield in practice should be over 85 per cent of theory.

The change of the sugars into alcohol and carbon dioxide is, unfortunately, only one of several reactions that occur during fermentation. Glycerol, fusel oil composed of higher alcohols, and succinic and pyruvic acids are produced in moderate quantity. Smaller amounts of formic, acetic, propionic, butyric, and lactic acids, aldehydes, and esters are also formed. The fusel oil comes from the decomposition of amino-acids.

The yeasts are uni-cellular vegetable organisms belonging to the genus Saccharomyces. They contain no chlorophyll and therefore, like other fungi, cannot live on the carbon in carbon dioxide as the plants do. In fact they manufacture this gas at the same time that they absorb oxygen. The yeasts that are cultivated are varieties of the species Saccharomyces ceverisiæ. Each fermentologist and plant manager cultivates a pet yeast of his own. This is always the best yeast in the world if one may believe the enthusiastic stories told about it.

Since yeast cannot assimilate carbon dioxide it must be provided with suitable nutrients in order that it shall grow and reproduce. Malt wort containing carbohydrates, phosphates, assimilable nitrogen compounds, and salts of potassium, calcium and magnesium has been found to be a satisfactory food for yeast.

To avoid the loss of sugar attendant upon the growth and catalytic effect of wild yeasts, molds, and bacteria, it is a common practice to make the saccharine liquid slightly acid with sulfuric acid before fermentation. The concentration of sugar is adjusted by dilution to such a point that the concentration of the alcohol formed during the earlier stages of the fermentation will not become great enough to stop the fermentation. The concentration of alcohol in the "beer" from the fermenters is 9 to 12 per cent by volume.

Fermenter rooms should be well ventilated, supplied with filtered or washed air, and lighted by weak diffused light. Cleanliness is essential to obtaining the best results.

The Manufacture of Alcohol from Cane-molasses.

The cheapest and most easily handled raw material for the manufacture of alcohol in the United States is cane-molasses. The sugar content of cane-molasses varies from 52 to 58 per cent when calculated as dextrose, and averages about 53 per cent for Cuban molasses. Each gallon of this molasses yields about 0.425 gallons of 95 per cent alcohol.

Cuban and Porto Rican molasses is shipped to deep-water points by rail or by lighter, and is then conveyed to the United States by tank-ship. The important alcohol plants, except those in Illinois, are located at Gulf or Eastern ports. The cost of a gallon of cane-molasses laid down at New York or Baltimore was normally 4½-5½ cents. Five cents is probably an average figure. The cost of the raw material for one gallon of 95 per cent alcohol is thus 11.75 cents. To this must be added the cost of yeast, malt, sulfuric acid, steam, water, labor, superintendence, plant overhead, revenue, red-tape, interest on investment, depreciation, and obsolescence. Before the war the cost of a gallon of 95 per cent alcohol was between 18 cents and 20 cents. At this time, on account of the higher price level for labor and commodities other than raw materials, it is probably 24 to 26 cents in a favorably situated and well managed plant.

Molasses from which alcohol is to be made requires no special treatment other than dilution in the proportion of 1 volume of molasses to 4 volumes of water, and slight acidification with sulfuric acid. The yeast, and yeast food in the shape of a malt infusion, are added, and the fermentation starts. Prior to the war the law specified that the fermentation vats could be charged only once in 72 hours. This led to the erroneous impression that this length of time was required. The rate of fermentation is independent of the concentration of sugar, but dependent on the concentration of yeast or the enzymes therefrom, and on the temperature. Temperatures of 75 to 80° F. are most favorable. During the war the restrictions on the use of the fermenting vats were removed, and the new regulations do not include any restriction. The time required is 30 to 40 hours.

The fermented mixture is pumped to the "beer" stills. If the "beer" is neutral these may be steel stills similar to those known to the Eastern oil-refiner as "cheese-box" stills. The largest stills of this type with which I am familiar are of 60,000 gallons capacity. "Beer" stills are usually operated intermittently. The vapors pass up through a dephlegmator or partial condenser, and then to a condenser. The "beer"-still serves to separate the alcohol from most of the water and organic matter whether dissolved or suspended. The product of the beer-still contains 45 to 50 per cent of alcohol by volume along with aldehydes, fusel oil, and smaller amounts of other volatil organic impurities. It is referred to as "low-wine." The residue from the "beer"-still is known as "slop," and its disposal constitutes one of the real problems that the alcohol manufacturer faces. The material may be evaporated, calcined, and the potash recovered. Other methods,

such as that of M. C. Whitaker [5] in which hydrofluosilicic acid is added, have been used. Decolorizing carbons are also produced from the slop. It is probably true at present that the alcohol manufacturer should feel well satisfied if any revenue derived from the slop is sufficient to pay the expense of disposal of the material. Further research work may quite change the story.

The "low-wines" are rectified to produce 95 per cent alcohol. Both batch and continuous stills are used to separate the alcohol from the water and impurities. The principles of the separation are essentially those of the separation of a binary liquid system showing a maximum on the vapor pressure curve. Reference should be made to Chapter V in this connection.

The first runnings from a batch-still contain volatil aldehydic and acidic impurities, and the last portion of the distillate contains the higher alcohols that compose the fusel-oil. Alcohol as thus made still contains small amounts of many impurities, that for some purposes should be, but seldom are, removed. Fuel alcohol is sufficiently pure when rectified in the ordinary manner.

References to several articles of interest in connection with the manufacture of alcohol from molasses are given herewith,[6] and in the bibliography at the end of the chapter.

Sources of Fuel Alcohol.

I have already pointed out that the real problem in the production of alcohol for use as a motor-fuel lies not in technology, but in finding a sufficient quantity of suitable raw material. In considering each material it is essential to keep in mind that it must be available in quantity at all times. Fruit of several kinds, for example, might be considered a suitable material from which to make alcohol. But it would be available for only a few weeks in years of crop abundance. A profitable business could not be built with so uncertain a source of raw material.

In passing it is interesting to note the materials currently used in the important alcohol producing countries. The United States uses molasses almost entirely, although some corn is used in the Middle-West. Prior to the war Germany produced 100,000,000 gallons of alcohol annually, of which more than two-thirds was made from potatoes, one-sixth from grains, and the balance from molasses, fruits, and miscellaneous materials. France produced 70,000,000 gallons of alcohol

[5] U. S. Patent 1,376,662, May 3, 1921, "Process of Obtaining Alcohol and Potassium Compounds."

[6] Owen, W. L., "Yield of Alcohol from Molasses from Different Sources." (Costs are also given.) *Sugar*, 16 (1914), 31-2. Herriot, T. H. P., "Molasses as a Source of Alcohol." *J. Soc. Chem. Ind.*, 34 (1915), 336-40. Foster, J. P., "Industrial Alcohol from Molasses." *Int. Sugar J.*, 21 (1919), 75. Little, A. D. Inc., "Molasses." A bibliography of several hundred titles. (1920.) Anon., "Motor Fuel from Waste Molasses." *Sugar*, June, 1920, 335-7. Child, J. F., "Motor Alcohol from Molasses." *Louisiana Planter*, 64 (1920), 381-2. Deming, E. W., "Production of Alcohol on Sugar Estates." *Louisiana Planter*, 66 (1920), 221.

in 1913 of which two-thirds, approximately, was made from sugar beets, and the rest from molasses, grains, and fruits. In the British Isles grain and molasses are largely used, in Russia potatoes and rye.

In the following paragraphs I shall briefly discuss the several raw materials that have been suggested from time to time as possible sources of fuel alcohol.

Cane-molasses.

The world's production of sugar has in late years approximated 40,000,000,000 lbs. Of this total cane sugar approximately 1/3 is consumed in the United States.

It will never be possible for the alcohol manufacturers in this country to control the molasses from all of this sugar. In fact, it would take very energetic management to control the molasses from 1/3 of the total cane sugar, but for the sake of the calculation let us assume that the molasses from 8,000,000,000 pounds of cane sugar would be available for use. The average yield of sugar from cane is 10 per cent. Hence to obtain 8 billion pounds of sugar it would be necessary to handle 80 billion pounds or 40,000,000 tons of cane. The yield of molasses varies from four to six gallons per ton of cane crushed. Assuming an average yield of five gallons molasses per ton of cane the total available quantity of molasses would be 200,000,000 gallons. From this molasses 85,000,000 gallons of 95 per cent alcohol would be made. This is less than 4.5 per cent of the present motor fuel requirement of the country, and is roughly equal to the largest quantity of alcohol produced in any year in this country from all raw materials. The inevitable conclusion is that cane-molasses will not be available in sufficient quantity to greatly increase the supply of motor fuel.

Beet-molasses.

Beet-molasses contains from 48 to 53 per cent of sucrose, averaging about 50 per cent. The theoretical yield of 95 per cent alcohol is 0.508 gallons per gallon of molasses. The yield in practice is about 0.4 gallon of 95 per cent alcohol per gallon of molasses.

Normally the molasses obtained in beet-sugar manufacture is treated by the Steffens process for recovery of 80 to 90 per cent of the sucrose contained therein. However, some plants sell or use the molasses as a stock-feed. The Steffens plant is looked on as a necessary evil by the beet-mill manager, and it is entirely probable that some manufacturers would be willing to sell the molasses at a price that might not equal the return from the Steffens plant. At 5 cents per gallon the beet sugar manufacturer would be netting a clear profit of 1 cent per pound for each pound of sugar that he could recover by running the Steffens plant. However, it is probable that buyers for feeding purposes will be able to outbid the alcohol manufacturer and that between this competition and the Steffens process there will be little beet-molasses used in making fuel-alcohol. The Western Industries Company of Agnew,

California, is the only concern, to my knowledge, that makes alcohol from beet-molasses in the United States.

Corn.

Corn contains an average of 63 to 65 per cent of starch, 2.0 per cent sugars, and 5.0 per cent pentosans. However, the better grades of corn cannot be used for alcohol manufacture because of their greater value for feed and food. The poorer grades contain not over 65 per cent of total carbohydrate substances. The yield of alcohol in practice is 95 gallons of 95 per cent alcohol per 2000 lbs. of corn. This is equivalent to 2.65 gallons per bushel, and is about 90 per cent of the theoretical yield.

The price of corn f.o.b. works at Peoria, Illinois, was 40 to 45 cents per bushel over a period of years before the war. The present price level of raw materials in general is 25 to 30 per cent above that of 1913. However, economists tell us that we have entered a new economic cycle in which falling prices may be expected for twenty or thirty years, although the broad tendency will be influenced by the periodic shorter cycles of prosperity and depression. Therefore, prices of 40 to 50 cents per bushel may perhaps be considered reasonable, and used as the basis of calculations. The raw material cost for the production of one gallon of 95 per cent alcohol from corn at 50 cents per bushel is 18.9 cents. This compares to 12.2 cents from cane-molasses at 5 cents per gallon f.o.b. alcohol plant.

If any of the grains are to be used for alcohol manufacture in this country corn will be the one. It is, therefore, of interest to inquire as to how much corn would be required and how much land necessarily devoted to the culture of enough of this grain to add substantially to the supply of motor-fuel. Assume that 1,500,000,000 gallons of alcohol could be made from 567,000,000 bushels of corn. If thirty bushels is taken as an average yield per acre it would require 18,900,000 acres to grow the corn necessary to produce this quantity of alcohol. This in only about 3 per cent of the total improved farm land in this country, and it may appear, therefore, that the production of corn for the manufacture of alcohol in large quantities is entirely possible. However, this conclusion must not be too hastily reached. A price of 50 cents per bushel for corn can hardly be regarded as attractive to the farmer, and yet the price must be such as to interest him if the grain is to be produced. This may be remedied in part by higher prices for motor-fuel, thus allowing of the payment of a better price for corn. It is quite out of the question to consider corn grown for food and feed, and that grown for alcohol manufacture, separately. Not only is the demand for food- and feed-stuffs of the United States to be reckoned with, but that of the entire world must be considered. The balancing of the economic forces might be favorable to the alcohol manufacturer for several years, when suddenly conditions would be reversed through crop failure. It is very difficult, indeed, to picture a stable alcohol industry based on a raw material for which there is sure

to be a prior demand at times. A further factor must also be taken into account. Corn grows to best advantage in this country in a fairly restricted area known as the corn-belt. Here climatic conditions are most favorable. While 3 per cent of the improved acreage of the country may seem a reasonable area to devote to increasing the corn crop, the 3 per cent must in truth be mainly within the corn-belt. The farm land of Illinois, Iowa, and Eastern Kansas is the most valuable that is devoted to the growing of cereals. So, although on superficial inquiry it may seem entirely possible to grow the necessary corn, further study of the problems suggests complicating factors. The balancing of the forces is not easy to foresee, but in my opinion only a gradual increase in alcohol production from corn can be expected. Possibly 200,000,000 gallons may be so made annually, ten to twenty years hence.

Potatoes.

Although potatoes have been the source of the larger part of the fuel-alcohol made in Germany, there appears to be little chance that they will be an important raw material in this country. Potatoes average about 19 per cent starch. The theoretical yield is 1.72 gallons of 95 per cent alcohol per 100 pounds of potatoes, but the average yield in practice is only 1.3 gallons. This is equivalent to 26 gallons of 95 per cent alcohol per ton, or 0.78 gallons per bushel. With potatoes at 25 cents per bushel the cost of the raw material for 1 gallon of alcohol is 32 cents. Even with potato culls at 15 cents per bushel the cost of the raw material is 19.2 cents. Potato alcohol, therefore, seems quite out of the question in this country. The use of potatoes in Germany is in part the result of Governmental aid in the form of premiums paid on potato alcohol, and in part of the peculiar industrial organization of the alcohol industry in that country. The average yield of potatoes per acre in Germany in 1913 was 235 bushels as compared to 90.4 in the United States in the same year.

Sweet Potatoes.

Sweet potatoes contain an average of 22 per cent starch and 6 per cent sugars, and will yield about 35 gallons of 95 per cent alcohol per ton. The use of sweet potatoes as a raw material for alcohol manufacture in this country appears improbable.

Sugar Beets.[7]

The average sucrose content of sugar beets is 15 per cent. The theoretical yield of 95 per cent yield is 25.7 gallons of 95 per cent alcohol per ton. The average yield in practice is 18.5 gallons per ton of beets. Under pre-war condition $5.50 per ton was a fair average

[7] Moorhouse, L. A., and Nuckols, "Cost of Producing Sugar Beets in Utah and Idaho, 1918-1919." U. S. Dept. Agr., *Bull. 963*, Sept., 1921. Townsend, C. O., "Sugar Beet Growing Under Humid Conditions." U. S. Dept. Agr., *Far. Bull. 568*, 1920. Beet Crop Estimate, U. S. Dept. Agr., 1919.

price for beets. The raw material cost on this bases for 1 gallon of 95 per cent alcohol is 29.8 cents. The use of beets in alcohol manufacture would be unsatisfactory on account of the short season in which the crop would needs be handled. The "campaign" in the average beet-sugar mill is three months—October, November, and December. If the beets become soft the extraction of the sugar by diffusion is difficult and expensive. All things considered I am of the opinion that alcohol will not soon be produced in large quantity from beets.

Artichokes.

The Jerusalem artichoke tuber contains 16 to 18 per cent of fermentable carbohydrates mainly in the form of levulose and inulin. The inulin is readily converted into levulose by boiling under pressure. The yield of 95 per cent alcohol per ton of tubers is about 22 gallons. The Department of Agriculture states that artichokes keep well and deserve attention as a possible source of alcohol.[8]

Cassava.

The cassava is a semi-woody shrub that grows to a height of 5 to 8 ft., and that develops tubers a foot or two long that weigh 8 to 10 lbs. The tubers are of a brownish yellow color, and contain a poisonous juice. Upon heating, the juice evolves hydrocyanic acid. There are two species of cassava, the bitter (Manihot utilissima) and the sweet (M. aipi). The former is cultivated in South America and the West Indies for the production of cassava flour and the tapioca of commerce. If 28 per cent of the root is assumed to be fermentable, a ton of roots should produce 39 gallons of 95 per cent alcohol.[9] At $9.75 per ton of tubers the cost of the raw material for a gallon of alcohol would be about 25 cents. The cassava may be worthy of study.

A number of tropical or sub-tropical materials have been suggested as possible sources of alcohol. Among these may be mentioned the Zamia Palm (Macruzamia) of Australia, New South Wales, and Queensland, and the Grass-tree (Genus Xanthorrhœa) of Australia. For a discussion of these reference should be made to *Bull. 20* of the Institute of Science and Industry of Australia, pp. 32-6. The Nipa-palm grows abundantly over large tracts in the Philippine Archipelago. It has been estimated that 50 million gallons of alcohol could be produced annually from this source. The flowers of the Mahua tree (Bassia Latifolia) are available in large quantities in Hyderabad according to the Nizam of Hyderabad.[10] The sun-dried flowers contain 60 per cent of fermentable sugars, and can be collected and baled for $7.25 per ton. The theoretical yield of 95 per cent alcohol is about 93 gallons per ton of flowers. If the practical yield were 80 per cent of this the raw material cost would be roughly 10 cents per gallon.

[8] U. S. Dept. Agr., *Bull. 429*, 18.
[9] *Bull. 20*, Inst. Sci. & Ind. of Australia, 30-1.
[10] B. Redwood, *Chem. Age*, 1 (1919), 66-8.

Trade wastes may be available in some localities. An example of this is corn-cannery waste, that may amount to 40 per cent of the weight of corn brought to the cannery (not counting the husks that are nearly one-third of the weight of the corn). Ten gallons of alcohol can be made from this waste for every ton of corn brought to the cannery. This is equivalent to about 27 gallons of alcohol per ton of waste excluding husks.

Most of these miscellaneous sources of alcohol should be disregarded in considering large scale alcohol production over the next decade or two. It is entirely possible that the tropical regions with their abundant sunshine, warmth, and moisture are the proper place for the growth of vegetation to yield carbohydrates or celluloses in quantity. This matter should be carefully studied, as in it may lie the solution of the fuel problem.

Sulfite Liquor as a Source of Alcohol.[11]

In the manufacture of sulfite paper-pulp a waste liquor that contains sugars is obtained from the digesters. These are fermentable, and alcohol can be produced therefrom. There are two pulp mills in this country making alcohol in this way, although it is problematical whether this is an economical procedure.

According to R. H. McKee[12] the usual procedure is to heat the sulfite liquor with lime sludge, filter off the precipitate of calcium sulfate and sulfite, and ferment the neutral liquor. The alcohol so produced contains up to 3 per cent of methyl alcohol and is purified with difficulty.

A process has been developed by Dr. McKee in which air is bubbled through the liquor to counteract the reducing action of the sulfur dioxide. The process is in use at the plant of the Hammermill Paper Company at Erie, Pa. The hot sulfite liquor (1400 to 2000 gallons per ton of pulp) is boiled in a preliminary treatment tank for about 5 hours, during which time air is bubbled through the liquor. The material is then cooled to 29° C., when it is run to the fermentation tanks. Yeast and yeast foods such as ammonium sulfate and calcium acid phosphate are added, and the liquor fermented. The cost of one gallon of 95 per cent alcohol varies from 18 to 30 cents depending on the glucose content of the waste liquor. The yield of alcohol averages 18 gallons per ton of paper-pulp. There are 95 mills in the United States producing a total of 1,500,000 tons of sulfite pulp annually. If all of these should make alcohol the quantity produced each year would be 27,000,000 gallons.

Miscellaneous Materials Yielding Carbohydrates.

Wheat, barley, rye, and other grains can hardly be considered as sources of fuel-alcohol in the United States. Their value for food and feed is too great.

[11] See Bibliography by A. D. Little, Inc. (1919), Shenard & Blanco, Paper, July 2, 1919.
[12] *Chem. Met. Eng.*, 21 (1919), 557-9.

Apples, peaches, apricots, pears, grapes and other fruits may be available in such abundance in occasional instances that no market is to be found. In such event they could be used in the manufacture of alcohol. These occurrences are so rare that it is unthinkable that an industry could ever be dependent on raw material of this nature and still succeed.

According to information in *Farmer's Bulletin 429* of the U. S. Department of Agriculture the sugar content of the common fruits is as follows:

Kind of Fruit	Average Per Cent of Total Sugars Calculated as Dextrose
Apple	12.2
Banana	13.8
Grape	15.0
Orange	5.4
Peach	7.6
Pear	10.0
Pineapple	11.7
Tomato	2.0
Watermelon	2.5

Ethylene as a Source of Alcohol.

Ethylene and propylene are olefins that are always present in gases formed when hydrocarbons are thermally decomposed. Pressure-still gas, vapor-phase cracking plant gas, coal gas, and coke-oven gas, all contain ethylene and propylene. The knowledge that ethyl and propyl alcohols could be made from these gases is very old, indeed. In 1827 Henry Hennell communicated to the Royal Society that he had identified "sulphovinic" acid in sulfuric acid that absorbed 5 per cent its weight of ethylene and had been given to him by Faraday. Berthelot in 1854 made ethyl alcohol from ethyl sulfuric acid. These observations and others that followed them have not been utilized commercially until recently because the demand for alcohol was not sufficiently urgent. The development of pressure-still cracking and vapor-phase cracking has resulted in the production of large quantities of by-product gas containing ethylene and propylene. Pressure-still gas contains about 10 per cent of olefins. Vapor-phase cracking plant gas may contain as much as 40 to 45 per cent of these gases.

A small plant was built by C. Ellis near the Bayway plant of the Standard Oil Company of New Jersey, and in which pressure-still gases were treated for the production of isopropyl alcohol. Ellis has described the operations and the information given here is taken from his article.[13]

The gas from the Burton stills is available at 90 pounds pressure, and has the following composition:

[13] *Chem. Met. Eng.*, 23 (1920), 1230. *Pet. Mag.*, Jan., 1921, 40-41, 156-8.

	Per Cent
Available Olefins	5
Ethylene	2–3
Hydrogen Sulfide	1

The hydrogen sulfide must be removed since it reacts with the sulfuric acid causing dilution of the acid, precipitation of sulfur, and formation of SO_2, and because bad-odored compounds are formed that make the alcohol hard to refine. Ellis does not state how the hydrogen sulfide is removed. The process used at Skinningrove in Great Britain consists in passing the gas through washers containing SO_2 in solution. The SO_2 is washed from the purified gas by water.[14] The purified gas is then brought into contact with sulfuric acid of 1.8 sp. gr. (about 87 per cent H_2SO_4) in batch absorbers or in towers. If the temperature rises above 20° C. polymerization of the olefins occurs. Hence a refrigeration plant is required to control the temperature in the absorbers. The specific gravity of the acid containing the alkyl esters is about 1.4, and the increase in volume resulting from the formation of esters, alcohols, and polymers, is about 80 per cent. Several hours are required to saturate the acid with olefins in a batch absorber. The product, a brown syrupy mixture, is mixed with several volumes of water. Oils and alcohols not soluble in water are separated, and the diluted acid solution is distilled in a lead-lined still. A crude 20 per cent isopropyl alcohol is then made, which is concentrated by distillation. The dilute sulfuric acid is concentrated and used again. The plant at Bayway has been taken over and enlarged by the Standard Oil Company of New Jersey. The isopropyl alcohol is sold under the name of "petrohol."

Ellis comments unfavorably on the manufacture of ethyl alcohol from ethylene. Strong sulfuric acid and high temperatures are required. Under these conditions polymerization, carbonization, and other difficulties are encountered.

C. F. Tidman, in the article already referred to, describes the manufacture of ethyl alcohol from coke-oven gas containing less than 2 per cent of ethylene. Temperatures between 60° C. and 80° C. are found to be the best. Sulfuric acid of 95.4 per cent strength is used. The absorption product contains free ethyl alcohol, sulfuric acid, ethyl hydrogen sulfate, and diethylsulfate. The free alcohol is sometimes as much as 50 per cent the total yield. Before distillation the acid is reduced to 64 per cent H_2SO_4 content. A vacuum of 26½ in. is used during the distillation. The initial temperature is about 94° C. and the final only 146° C., no frothing occurs, and the acid, freed from alcohol, contains 80 per cent H_2SO_4. The distillate produced contains about 15 per cent alcohol. About 1.6 gallons of 95 per cent alcohol is made per ton of coal carbonized.

[14] Tidman, C. F., "The Manufacture of Alcohol from Coke Oven Gas." *J. Soc. Chem. Ind.*, 40 (1921), 86T-89T.

As the situation stands today it appears that the production of isopropyl alcohol is a feasible commercial operation, while that of ethyl alcohol is problematical. The broader use of cracking processes may ultimately lead to the manufacture of both alcohols, but even so, the quantity of alcohol that could be so made would be no more than a substantial addition to the fuel supply. One hundred million gallons might be produced if the matter were energetically pushed. Further references to articles on this subject are given herewith.[15]

Acetylene as a Source of Alcohol.

A process has been developed in Switzerland[16] for the making of alcohol from lime and coke. Calcium carbide is first produced and this is hydrolyzed with water to produce acetylene. From acetylene it is possible to make alcohol in either of two ways. The acetylene may be catalytically reduced with hydrogen to make ethylene, and this in turn converted into alcohol; or the acetylene may be hydrolyzed to acetaldehyde and this catalytically reduced to ethyl alcohol. The latter method is the one that is followed. With calcium carbide costing $30 per ton, as it does at Niagara Falls where power costs $16 per horse power year, the cost of the raw material (calcium carbide) for alcohol would approximate 15 cents per gallon of 95 per cent alcohol.

There is apparently little advantage over grain in so far as cost of raw material is concerned. The main interest in the method lies in the fact that the raw materials consumed are well nigh inexhaustible, and that, given reasonably cheap power, this method can compete with other methods. Power is not to be had in unlimited quantity, but there are localities in this country where large developments of reasonably cheap power are possible.

One concern in Canada, The Canadian Electro Products Company of Shawinigan Falls, is in a position to make alcohol in this way. They produce carbide and acetaldehyde. So far as I am aware they have been making all of their acetaldehyde into acetic acid, but at any time that it should seem wise to do so they are in a position to make alcohol.

An extensive development of this method of producing alcohol I regard as unlikely so far as the immediate future is concerned in this country. But it is easily within the range of future possibility.

Alcohol from Wood.

The manufacture of ethyl alcohol from wood and other cellulosic and lignocellulosic materials has engaged the attention of chemists for more than a century. Yet, today, only two plants are considered com-

[15] Curme, Jr., Geo. O., *Chem. Met. Eng.*, 25 (1921), 907-9, 957-59, 999-1000, 1049-50. "K"—*Chem. Age* (Lond.), 4 (1921), 440-3. Plant and Sidgwick, *J. Soc. Chem. Ind.*, 40 (1921), 14-18T. deLoisy, E., *C. r.*, 170 (1920), 50-3. Bury, E., Ollander, O., *Gas J.*, 148 (1919), 718-21. *Chem. Tr. J.*, 66 (1919), 36-7. Bury, E., *Gas Wld.*, 73 (1920), 23-5. *Gas J.*, 151 (1920), 449-50.

[16] Kent, W. P., Commerce Reports, 1917, 102, 426.

mercially successful, and the success of these in the competitive market of the moment is questionable. One of these plants, with a capacity of 2500 gallons of alcohol daily, is operated by the duPont Company at Georgetown, South Carolina, the other with a daily capacity of 2000 gallons is located at Fullerton, Louisiana.

The manufacture of alcohol from wood depends on the hydrolysis of part of the cellulose, by means of dilute acid under about 60 lbs. steam pressure, to a mixture of pentose and hexose sugars. The latter are then fermented to alcohol. In practice 12 to 20 gallons of 95 per cent alcohol are obtained per ton of wood, although in the laboratory yields of 35 to 40 gallons per ton of wood have been obtained. Some woods yield much more alcohol than others.

Were it not for the fact that the manufacture of alcohol from wood has been made the subject of a recent Government Bulletin,[17] written by Dr. Kressmann, I should feel constrained to review the subject in some detail. The importance of developing an industry that produces alcohol from wood cannot be overestimated.

Dr. Kressmann compares the several methods that have been tried, discusses the availability of the raw-material, the costs, investigational work, fermentation, and by-products, and gives a list of the important patents and technical articles dealing with the subject. The reader is referred to this valuable one-hundred page bulletin.

I have long been of the opinion that the development of an alcohol industry, on a scale comparable in any sense with the petroleum industry, was contingent upon the use of wood as a raw material. The yield of alcohol in practice is so far from the theoretically possible yield that it must surely be difficult for anyone of scientific bent to believe that great improvement cannot be made. A recent article by R. C. Hawley[18] entitled "The Forests of the United States as a Source of Liquid Fuel Supply" has interested me and deepened my conviction that within a decade or two alcohol from wood will be a reality in a large way. Some of the salient facts of this article are reproduced in the accompanying tables and notes on page 502.

Of this total, 4,800,000,000 cu. ft. cut for lumber are lost through waste in the woods and at the mills. The possible annual growth as shown in Table LXXII exceeds the total cut as shown in Table LXXIII by 1,750,000,000 cu. ft.

If a cubic foot of wood is taken as weighing 30 lbs. and the assumption is made that each ton of wood will yield 15 gallons of 95 per cent ethyl alcohol, the annual output of fuel from the 11,030,000,000 cu. ft. of wood would be 2,482,000,000 gallons.

The possibilities of growing forest crops for the production of fuel-alcohol are shown in the following three examples.

I. Hardwood in Connecticut.—The forests of Connecticut are of mixed hardwood character, the principal species being oak, hickory,

[17] U. S. Dept. of Agr., *Bull. 983*. "The Manufacture of Ethyl Alcohol from Wood Waste." Apr. 6, 1922.
[18] *J. Ind. Eng. Chem.*, 13 (1921), 1059-60.

TABLE LXXII

AREA AND GROWTH OF FORESTS IN THE UNITED STATES *

Area Forested Acres	Character	Present Annual Growth, Cu. Ft.	Possible Annual Growth, Cu. Ft.
245,000,000	Second growth Forests.	5,995,000,000	14,700,000,000
81,000,000	Waste Land on which nothing is growing or is likely to grow without reforestation.	None	4,860,000,000
137,000,000	Virgin Forests.	None	8,220,000,000

* All figures are from "Timber Depletion, Lumber Prices, Lumber Exports, and Concentration of Timber Ownership," Forest Service Report on Senate Resolution 311.

TABLE LXXIII

AMOUNT OF WOOD REMOVED ANNUALLY FROM THE FORESTS OF THE U. S.

Cut	Cu. Ft.
Lumber	8,913,300,000
Fuel Wood	10,450,000,000
Other Products	4,955,615,000
Destroyed by Fire, Insects and Fungi	1,730,000,000
Total	26,048,915,000

TABLE LXXIV

WOOD AVAILABLE FOR MANUFACTURE OF ALCOHOL WITHOUT ENCROACHING ON THE SUPPLY OF OTHER FOREST PRODUCTS

Source	Cu. Ft.
Waste in Woods and at Mills	4,800,000,000
Losses from Fire, Insects and Fungi (taken out in thinnings)	1,730,000,000
Excess of Possible Growth Over Current Requirements (taken out in thinnings)	1,750,000,000
Intensive Growth Resulting from Better Management (taken out in thinnings)	2,750,000,000
Total	11,030,000,000

birch, maple, and ash. They cover an area of 1,500,000 acres, and are capable of producing not less than 67,500,000 cu. ft. per year. One-third of the growth could be removed each year in thinnings and converted into alcohol. At present this class of material is not utilized. Connecticut hardwoods are estimated to average 40 pounds to the cubic foot, and to yield 10 gallons of alcohol per ton of wood. On this basis the 22,500,000 cu. ft. would yield 4,500,000 gallons of alcohol annually. The cost of the raw wood laid down at the plant is estimated at 28 cents per gallon of alcohol.

II. Short Leaf Pine in Virginia.—Short leaf pine is one of the Southern pines and has a commercial range of more than 150,000,000 acres within the Southern States. It would be an excellent tree to grow as a crop for conversion entirely into liquid fuel. A 25-year rotation shows a wood production of 208 cu. ft. per acre per year. Allowing a weight of 30 pounds per cubic foot of wood, and 20 gallons of alcohol per ton of wood, the annual yield per acre would be over 62 gallons. The cost of the raw wood laid down at the plant should not exceed 7 cents per gallon of alcohol. For an annual production of 1,000,000 gallons of alcohol, to be maintained indefinitely, 16,129 acres of land would be required. Approximately, 645 acres would be cut clear each year. Each acre when cut clear would yield 5,220 cu. ft. of wood, or 1,566 gallons of alcohol.

III. Douglas Fir in Western Oregon or Washington.

West of the Cascade Mountains, in Oregon and Washington, Douglas Fir is the chief commercial species and is used largely for lumber. Approximately 15,400,000 acres west of the Cascades are non-agricultural lands suitable for growing Douglas Fir.

On an 80-year rotation for lumber as the chief product, the annual production of these lands is estimated at over 2,000,000,000 cu. ft., of which 800,000,000 cu. ft. could be removed annually in thinnings. Allowing 30 lbs. per cu. ft. of wood, and 20 gallons of alcohol per ton of wood, the annual production of alcohol from wood taken out as thinnings would total 240,000,000 gallons.

If it is desired to grow Douglas Fir as a crop for complete utilization in the manufacture of fuel-alcohol a 40-year rotation should be used. On the better-grade lands 275 cu. ft. of wood could be produced per acre each year, or 82.5 gallons of alcohol. The cost of the wood laid down at the plant should not exceed 9 cents per gallon of alcohol. An annual production of 1,000,000 gallons of alcohol could be maintained indefinitely from 12,121 acres of land. Approximately, 303 acres would be cut clear each year, and each acre would yield 11,000 cu. ft. of wood or 3,300 gallons of alcohol.

While these are large operations they are not of such magnitude as to be impossible.

Summary of the Future Possibilities of Fuel Alcohol.

The value of alcohol as a fuel has been amply demonstrated. It is probable that it will be consumed as a component of mixed fuels.

Alcohol can be made from a great variety of materials. At present and in the near future it will be produced mainly from cane-molasses. Corn is the next most likely starchy or sugary material. Other grains are scarcely to be considered as sources of fuel alcohol. Moderate quantities of propyl and ethyl alcohols may be made from the olefinic gases that are by-products of cracking operations. All told it is improbable that more than 500,000,000 gallons of alcohol can be produced from all of these sources. The raw materials of the tropics are not well enough known to enable one to judge their future possibilities with any accuracy.

Wood appears to be the most likely future raw material, and with the technical developments that may be confidently expected, large quantities of alcohol will be produced from this material.

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Chapter XIII.

Composite and Miscellaneous Motor Fuels.

The production and distribution of composite fuels, although as yet a small industry, is assuming a position of increasing importance. War-time demands for benzene and toluene led to great expansion of facilities for the production of the lower-boiling aromatic hydrocarbon distillates, and it is only natural that a part at least of these facilities should now be utilized in making aromatic distillates for use as motor fuels. Leaders in the alcohol industry have long been cognizant of the probable future use of alcohol as a motor fuel. However, the automobile of today is equipped with carburetion devices and power-plant designed to use gasoline and not benzene, toluene, or alcohol as fuel. The logical outcome of the situation has been the development of composite fuels that can be used satisfactorily in present automotive equipment, and thus furnish an outlet for the benzene, alcohol, or other combustible liquid now available.

It is not my purpose to discuss the utilization of the composite fuels, except in passing, but I do wish briefly to call attention to the general lines of development. Also, for want of a better place, I shall include a brief discussion of such miscellaneous materials as may be of some future importance as motor fuels.

The most important group of composite fuels are those containing alcohol. At the moment more fuels containing benzene and other aromatic distillates may be marketed, but these mixtures, while of some commercial importance, will never be of great importance because of the limited quantity of these materials available.

Fuels composed of gasoline blended with alcohol, with aromatic hydrocarbons or with both possess one important advantage over gasoline that might not be anticipated, namely, their combustion is not attended by the fuel-knock. This subject has been studied by the Research Division of the General Motors Company. Some of the preliminary results are reported by T. Midgley, Jr., and T. A. Boyd.[1] Reference should be made to the original paper for details, but a few of their findings can be given here. Alcohol was more effective than benzene, toluene, or xylene in suppressing the fuel-knock. For example 35 per cent by volume of alcohol was equivalent for this purpose to 55 per cent by volume of benzene when each was blended with kerosene. When the composition of the component fuels was expressed in terms of molecules, rather than volumetric per cents, alcohol still showed superiority over benzene. Xylene is more effective than toluene, and toluene more effective than benzene in suppressing the fuel-knock.

[1] *Nat. Pet. News,* July 5, 1922, 59-60, 63-64, 67-68.

Composite Fuels and Patents.

Numerous patents have been issued covering motor-fuel compositions, in this and in foreign countries. The subject has recently been discussed by W. R. Ormandy [2] in a paper before the Institution of Petroleum Technologists. To put it briefly Dr. Ormandy is of the opinion that many of the currently issued patents are not worth the paper they are printed on because the supposed disclosures have long been common knowledge. Patents have been granted for the admixture of substances that every chemist knows will mix, and that every engineer knows will burn. He states that between the years 1900 to 1910 he tried all sorts of mixtures of fuels containing gasolines, kerosenes, benzene and other aromatic distillates, alcohol and ether, though, in his own words, "I never contemplated the possibility of taking out a patent for admixtures which it was perfectly obvious to anyone with an elementary chemical knowledge could be employed if the ingredients thereof were obtainable in sufficient quantity at a reasonable price. Many of the patents which have been referred to are certainly not inventions or discoveries. I assume that if one applied for a patent for the utilization of the chemical substance H_2O, either alone, or in conjunction with small quantities of alcohol, as a beverage, that it would be rejected on the grounds that it was public knowledge at the time the application was made. It is equally public knowledge to anyone skilled in the art in question that such liquids as paraffin, petrol, benzol, alcohol, ether, acetone, will either mix in any proportion, or in restricted proportions, and that by admixture, for example of petrol with benzol, a certain amount of alcohol can be caused to dissolve in the mixture which would not dissolve in petrol alone. It is equally common knowledge to chemists and engineers that any admixture of two or more volatil fuel bodies will result in a third substance also capable of being used as a fuel."

Possibly the experience and opinions of others are similar to those of Dr. Ormandy. Doubtless, others still will not agree. It is not my purpose to enter into a discussion of the patents on composite fuels, for these are numerous and their value is not to be judged on technical grounds alone. Ormandy's views refer to British patents, although possibly they are just as applicable to United States patents. The matter is one that should be given careful study before the production of composite fuels is undertaken by any organization, lest valid patents be infringed or production deterred by patents whose validity could not be sustained.

Composite Fuels Containing Ethyl Alcohol.[3]

The most important composite fuels from a commercial standpoint that contain alcohol are Alcogas and Natalite, the former manufactured

[2] *J. Inst. Pet. Tech.*, 6 (1920), 229-48.
[3] On this general subject see—Ormandy, W. R., "Motor Fuels, with Special Reference to Alcohol." *J. Roy. Soc. Arts.*, Feb. 6, 1914, 234. Lewes, V. B., "Motor Fuels." *J. Roy. Soc. Arts.*, July 9, 16, 23, 1915, 757, 773, 792.

by the U. S. Industrial Alcohol Company of New York and Baltimore, the latter deriving its name from the fact that it has been made from molasses at Natal, South Africa.

Alcogas.

Two types of Alcogas have been marketed, one for use in airplanes, and the other for use in motor vehicles. The Aviation Alcogas tested by the U. S. Bureau of Standards had the following approximate composition:

	Per Cent
Alcohol	40
Gasoline	35
Benzol	17
Other	8

Among the "other" components was a few per cent of ether.

Alcogas for automobile use has the following approximate composition:

	Per Cent
Alcohol	33
Gasoline	35
Benzol	25
Ether	7

The composition of these mixtures has not been blindly chosen, but is the result of careful study of limiting economic and technical factors. The primary motive of the manufacturers of Alcogas is to furnish an outlet for all alcohol that cannot be sold at prices higher than that obtainable for fuel. If fuel is to be made and sold, it should therefore contain as much alcohol as is possible without so changing the characteristics of the product as to make it difficult to use it interchangeably with gasoline of current market grade. Alcohol alone cannot be so used. Hence the necessity for a blended product. The logical procedure is to mix alcohol and gasoline, but unfortunately these liquids are not completely miscible. The less the water content of the alcohol, the larger the proportion of it that can be blended with gasoline. But alcohol stronger than 95 per cent is too expensive to produce for use as fuel, hence the necessity of a blending agent. Aromatic distillates and ether are both suitable. Cost, again, is the main factor determining choice. If benzol, toluol, or xylol are obtainable at prices that allow of lowering the cost per unit volume of fuel they will be used, for in addition to being cheap they are good fuels and tend to reduce the tendency to knock. This is of special importance in making Alcogas for automobile use since in the warmer season of the year part of the gasoline can be replaced with kerosene, thus lowering the unit cost of

the fuel-mixture. Kerosene alone knocks badly, but when blended with alcohol and benzol, in amounts such as are used in making motor Alcogas, the difficulty is eliminated. Ether is a much more effective blending agent than the lower-boiling aromatic hydrocarbons, but is somewhat more expensive, and is of itself a knock-producer.[4] With alcohol costing the manufacturer of ether 20 to 25 cents per gallon it should not cost more than 50 to 60 cents per gallon to produce crude ether. The small amount of ether that is necessarily used in blending 95 per cent alcohol and gasoline will not cause difficulty on account of its own tendency to knock when burned as a motor fuel. The presence of a few per cent of ether is desirable, as the starting properties of such a mixture are much better than those of a similar mixture not containing ether. It is worthy of note that if alcohol becomes an important motor fuel the use of aromatic distillates as blending agents will be quite out of the question, since they will not be available in sufficient quantity. Ether will then be used. The cost situation will also be different then because it is difficult to see how a large alcohol industry can be established until the price of gasoline is over 35 cents per gallon. The composition of Alcogas as given above must not be interpreted as being exact. Rather, Alcogas should be considered as containing the given components in proportions that will be governed to a large extent by price. The analyses given are representative of the products marketed currently.

Tests conducted by the Bureau of Standards[5] showed that the thermal efficiency of an airplane engine was 15 per cent higher when using Airplane-Alcogas than when using airplane-gasoline. The density of the Alcogas was 12 per cent greater than that of the gasoline, and the gross heat of combustion of the Alcogas 106,000 B.t.u. per gallon as compared to 120,000 B.t.u. per gallon for the gasoline. The higher heating value of the gasoline is offset by the more efficient utilization of the Alcogas, so that volume for volume the effective or useful work obtainable is the same for both fuels. However, it was the opinion of the operating engineers that the engine ran more smoothly

[4] Baumé and others (*Chim. et Ind.*, 3 (1920), 761-68) show that the minimum temperature at which a homogeneous mixture of hydrocarbon, alcohol, and benzene (or ether) can exist, rises rapidly with increase in the water content of the alcohol. The solubility of alcohol in hydrocarbons of a given series decreases with increase of molecular weight of the hydrocarbons. At 0° C. heptane and absolute alcohol are miscible in all proportions, 95 per cent alcohol dissolves in heptane to the extent of 30 per cent, and 90 per cent alcohol to the extent of 17 per cent. All mixtures of alcohol and benzene containing more than 50 per cent of the latter solidify above 0° C. The volume of benzene necessarily added to mixtures of hydrocarbon and alcohol to cause complete miscibility increases with increase in molecular weight of the hydrocarbon. A mixture of 33 per cent of ordinary gasoline with 67 per cent of 95 per cent alcohol requires the addition of 15 per cent of benzene (at —5° C.), whereas if the gasoline is replaced by a very light petroleum distillate only 1.5 per cent benzene is required.

The solubility relationships of the system alcohol-water-ether has been investigated by Routin and Sanfourche (*Bull. Soc. Chim.*, 25 (1919), 458-63), at 15° C., by Horiba (*J. Tokyo Chem. Soc.*, 31, 944) at 25° C., and by Bonner (see *C. A.*, 5, 817) at 10° C.

[5] *J. Soc. Auto. Eng.*, 6 (1920), 397-401.

on Alcogas. The main advantage of Alcogas was the freedom from knocking at ground-level even when the compression-ratio was 7.2 and the throttle wide-open.

An important advantage of Alcogas over gasoline, noted in tests made by the U. S. Air Mail Service, was the 40 per cent lower consumption of lubricating oil, and the less dilution of the lubricating oil by Alcogas. In five hours of running, the oil used to lubricate a Hispano-Suiza engine was diluted only 0.97 per cent when Alcogas was used as fuel, but 6.3 per cent when gasoline was the fuel used.[6]

All tests with which I am familiar have shown that much less carbon is formed when airplane- or motor-Alcogas is used than when gasoline is used. The carbon formed when the composite fuel is used is softer and flaky. So far as I am aware no instance of corrosion by the combustion products from Alcogas has been observed.

Natalite.

Natalite is a fuel-blend of alcohol and ether, that was first produced in Natal, South Africa, in 1914. The proportions of the several components are variously stated to be within the following limits:

	Per Cent
95 per cent Ethyl Alcohol	54–60
Ether	45.8–39
Pyridin, ammonia, or trimethylamine	0.15–1
Denaturant (arsenious acid)	0.5

So far as I am aware Natalite has not been sold as a motor fuel in the United States, nor is it probable that it will be used here in place of blended fuels such as Alcogas. In localities where the hydrocarbon fuels are not available Natalite or some similar mixture should be commercially important. It is stated that Natalite can be used as a fuel with carburetors and engines designed to burn gasoline, that it does not cause corrosion, that it will not freeze at any temperature encountered in using fuels, that its use allows of easily starting the engine. and that it is generally satisfactory.

For more detailed information on Natalite the reader is referred to the references given in the footnote.[7]

[6] For further details see an article by B. R. Tunison, *Pet. Age*, July, 1921, 39.

[7] Greene, H., *Power*, 27, 328. "A New Fuel for Internal Combustion Motors." Ossa, Belisario Diaz., *Bol. soc. fomento fabril*, 35, 41-3. "A National Liquid Fuel." Hempel, W., *Z. Angew. Chem.*, 27 (1914), 521-2. Watson, W., et al., *Inst. Automob. Eng.*, Dec., 1914. "Benzene, Alcohol, and Mixts. of These Liquids with Petrol as Fuels for Internal Combustion Engines." Dieterich, K., *Z. Angew. Chem.*, 27 (1914), 543-4. "Benzine and Benzene Substitutes." Anon., *Chem. Tr. J.*, 56 (1915), 554. Anon., *Sugar J.*, 18 (1916), 32-3. "Natalite." Momsen, R. P., *Comm. Reps.* No. 193, Aug. 17, 1918, 652. "Brazilian Company to Mfg. Ethyl Gas." Humboldt, E., *Power*, 50 (1919), 418-20. "New Fuel Mixtures for Internal Combustion Engines." Purgotti, A., *Em. Biorn. chim. ind.*

Mixtures of Alcohol and Benzene.

Fuels composed of alcohol and "benzol" have been used to a small extent in Europe. As noted by H. B. Dixon [8] it is remarkable that although the vapor-pressure of pentane, hexane, and ether are lowered by admixture with alcohol, the vapor-pressure of alcohol-benzol mixtures is above that of either component alone. The vapor-pressures of the substances and of some mixtures as given by Dixon are shown in Table LXXV.

TABLE LXXV

VAPOR PRESSURE OF FUELS

Given in Millimeters of Mercury.

Temp. ° C.	Temp. ° F.	Ether	Natalite Ether 45 Alc. 55	Ether 20% Alcohol 80%	Alc.	Hexane 20% Alcohol 80%	Hexane	Benzene 20% Alcohol 80%	Benzene
0	32	180	165	73	14	30	44	37	28
10	50	280	250	105	22	46	76	56	45
20	68	433	380	162	42	80	121	90	75
30	86	637	547	247	79	141	184	142	120
40	104	...	...	350	135	219	276	215	180
50	122	...	...	500	217	328	400	325	263

No difficulty is encountered in starting a cold engine on a mixture of 20 per cent benzol to 80 per cent alcohol. Fuels composed of these liquids in various proportions have been proposed, studied, and used. G. J. Shave [9] states that after a month of use of a 50 to 50 mixture of alcohol and benzol the fuel tanks of London busses became porous. A tar-like deposit in the inlet-valve pockets was also observed. Engines using this type of blended fuel do not knock on the hills. By using lead-coated fuel tanks, and by providing for the cleaning of the engine periodically, satisfactory results were obtained.

The corrosive effect of alcohol-benzol mixtures is probably caused by the presence of acidic and aldehydic components, and suggests that alcohol might in some cases need refining with an alkali. This applies to alcohol used as a non-freeze also. While it is usually claimed that alcohol non-freeze is entirely non-corrosive this statement is not based on fact. A simple alkaline treatment will remedy the difficulty.

The gum-formation noted by the London Omnibus Company was probably caused by the presence of di-olefin compounds in the benzol.

applicata, 2 (1920), 191. "Employment of Alcohol in Explosion Motors." "Thernol." Anon., *Eng.*, 109 (1920), 150. "Fuel for Internal-Combustion Engines." Child, J. F., *La. Planter & Sugar Mfgr.*, June 12, 1920, 381-2. "Motor Alcohol from Molasses." Olmer, L. H., *Bull. Soc. Chim.*, 29 (1921), 382-5. "Vapor Pressure of Mixtures of 95 Per Cent Alcohol and Ether." Anon., *La. Planter & Sugar Mfgr.*, 66 (1921), May 14, 316-18. "Natalite and the World's Motor Fuel Position."

[8] *Aut. Ind.*, Feb. 3, 1921, 211-5.

[9] *Eng.*, 110 (1920), 623-4.

lar difficulty has been encountered in some instances in this country. ting with sulfuric acid will avoid the trouble.

'he system benzene-alcohol-water has been investigated between ;° C. and — 5° C. by N. V. Sidgwick and W. J. Spurrell,[10] and previous literature on this and the three possible binary-systems wed. The freezing point of mixtures of alcohol and benzene rises enzene is added. For example, a mixture of 45 per cent benzene weight) and 55 per cent of 95 per cent alcohol is in equilibrium the solid phase at — 5° C., while a mixture of 80 per cent benzene weight) and 20 per cent of 95 per cent alcohol is in equilibrium at ly less than + 2° C.

urther information on the use of alcohol-benzol mixtures will be d in the accompanying references.[11]

line-Benzene Fuels.

enzene, and other aromatic distillates not required for making osite fuels containing alcohol, should be marketed by blending with ine. A fuel of this type known as Signal Core Mixture has been l in the U. S. Bureau of Standards altitude laboratory. It con- l of 20 per cent by volume of "90 per cent benzol," [12] and 80 per of gasoline.[13] The fuel was found satisfactory although possessed marked advantage over gasoline. The following specification for or Benzol" is given [14] by Wm. Rile of the Barrett Company:

ic Gravity	0.878
r	0.25 per cent
on	Neutral
ation: 1st drop	79–80° C. or 175° F.
per cent below	100° C.
per cent below	121° C.
ry below	135° C.

o appreciable residue. Must pass doctor and gumming test.

he British Engineering Standards Association issues the following ication for "Benzol." [15]

efinition.—The term "benzole" shall denote a liquid consisting tially of a mixt. of benzene, and not more than 30 per cent by vol. uene and xylenes. *Description.*—The liquid shall be a clear "water-" liquid, free from undissolved water and other visible impurities.

J. Chem. Soc., 117 (1920), 1397-1404.
Ormandy, W. R., *Proc. Inst. Auto. Engrs.*, 1913-4. Dixon, H. B., *Aut.* Feb. 3, 1921, 211-5. Mohr, O., *Z. Angew. Chem.*, 27 (1914), I., 558-9.
ndy, W. R., *J. Inst. Pet. Tech.*, July, 1920, 238-9.
A mixture, 90 per cent of which distills below 100° C., and that contains per cent benzene, along with toluene and small amounts of the xylenes.
See "Power Characteristics of 20 Per Cent Benzol Mixture." *J. Soc. Eng.*, 5 (1919), 272-4.
Pet. Mag., 10, Mar., 1921, 129-31. *Power*, 52 (1920), 1034.
Auto. J., 26 (1921), 131.

Specific gravity.—The specific gravity at 15.5° C. shall be not less than 0.870, and not more than 0.885. *Distillation range.*—When 100 cc. of the material are distd. in the standard distn. app. (B.S. Specification, No. 2, D. 15), at a rate of 7 cc. per min. there shall distill at 760 mm. pressure: Not less than 60 cc. at or below 90°, not less than 75 cc. at or below 100°, not less than 90 cc. at or below 120°. The flask shall be dry at a temp. not exceeding 125° (257° F.). The temp. recorded by the thermometer shall be corrected for emergent stem and barometric pressure, by means of the formulas given in the appendix. *Residue.*—The amt. of non-volatil residue remaining, when 20 cc. of the material are evapd., and subsequently heated for 2 hrs. on a water-bath at 100°, shall not exceed 0.01 per cent by wt. *Coloration with sulfuric acid.*—The coloration imparted to pure H_2SO_4 (90 per cent H_2SO_4), free from HNO_3, when 90 cc. of the material are shaken with 10 cc. of the acid for 5 min., at ordinary temps., shall be not more than a light brown. *Sulfur content.*—The total sulfur content shall not exceed 0.4 per cent by wt. A convenient method for estn. of S. is given in the appendix. *Freedom from acid and alkali.*—The material shall give no reaction for free acid or free alkali, when tested by the method described in the appendix. *Freedom from hydrogen sulfide.*—The material shall give no reaction for H_2S when tested by the method described in the appendix. *Freezing point.*—The f.p. shall not be higher than 14° (7° F.) when detd. by the method described in the appendix. The appendices give details of: Method of testing for color; temp. corrections for emergent stem and barometric pressures; methods of testing for S. free acid or free alkali, H_2S, f.p.; and details of the standard distn. apparatus.

Benzol mixtures have been regarded as unsatisfactory by some, and as better than gasoline by others. Difficulties have been ascribed to sulfur, to gumming, and to carbon—probably with much truth in many instances. The truth is that benzol burns well in an engine under full load, but forms carbon under light load.[16] The carbon is not gummy like that formed when kerosene is burned, but is fluffy and more easily blown out by the exhaust gas. Benzol alone does carbonize the spark-plugs badly. However, a composite fuel containing 20 to 40 per cent of properly refined benzol and 80 to 60 per cent of gasoline is a satisfactory fuel that will show less tendency to knock than gasoline.

A mixture of 20 per cent benzol and 80 per cent cyclohexane has been patented by the General Motors Company and called "Hecter." The freezing points of benzene and cyclohexane are between 42 to 43° F., but that of "Hecter," the approximate eutectic mixture, is about —40° F.

Reference may be made to several articles other than those already cited on benzol and on fuel-mixtures containing benzol.[17]

[16] Kettering, *J. Soc. Auto. Eng.*, 4 (1919), 263-9.

[17] Grebel, A., *Le Genie Civil*, 53, 113-6; thru *Pet.* 3, 1131. Spilker, A., *Chem.-Ztg.*, 34, 478. Anon., *Gas Wld.*, 58, 175-6. Anon., *Chem. Eng.*, 18, 215-6. Foxwell, G. E., *J. Gas. Lt.*, 125, 292-3. Viala, F., *Bull. Soc. chim.*, 15, 5-11. Helfenberg, K. D., *Pharm. Post.*, 47 (1914), 183-9. Terres, E., *J. Am. Soc. M. E.*, 37

erosene-benzol Fuel-mixtures.

A mixture of kerosene and benzol called "Liberty" fuel has been nvented" by E. C. Weisgerber, and sponsored by the General Engi-ɜer Depot of the U. S. Army. Wherein lies the invention is difficult see, for such mixtures are "old as the hills." Various mixtures of ɜrosene and benzol are called "liberty" fuel. The chief difficulties ıcountered in using kerosene as a motor-fuel are carburetion and fuel-ıock. By mixing 20 per cent or more to benzol with kerosene these fficulties are avoided in some measure. The use of benzol in such a ixture is logical and justified so long as the benzol is not required ır the more valuable purpose of blending alcohol and gasoline.

The U. S. Bureau of Standards tested "Liberty" fuel, and found .at it could be used successfully in a Hispano-Suiza engine at a com-·ession ratio of 5.3 : 1.0. The power developed was equal to that ɜveloped when gasoline was used. The weight of fuel consumed per ·ake-horsepower-hour was about 3 per cent greater when "liberty" ıel rather than gasoline was used. As would be expected, because ıth kerosene and benzol are heavier than gasoline, about 5 per cent ss by volume of "liberty" fuel than gasoline was required per brake-ırsepower-hour. The engine developed 3 per cent more horsepower hen consuming 10 per cent greater weight of fuel per horsepower-ıur when the "liberty" fuel was used in place of gasoline.

hale-Oil.

I have briefly discussed the possibilities of shale-oil in Chapter I, ıd shall add but little here. Crude shale-oil contains a small per cent low-boiling hydrocarbons of poor quality. The heavier parts of the l are quite different in character from the petroleums as is indicated the work of Botkin.

Reams have been written on shale-oil,—so much, in fact, that one els that shale-oil is mostly talk and very little oil. Optimism has run ɔt. While I am sure that shales will eventually be important sources fuel-oils, I am equally sure that these developments are several ɜcades ahead. The job is too hard and too big, and the present need sufficiently urgent.

The reader should refer to Dr. Ralph H. McKee's recently pub-ʃhed book on this subject. Dr. Victor C. Alderson gives an optimistic cture of the present and future of the industry in his recent book on ıale-oil.

915), 46-8. Whitehead, S. E., *Gas J.*, 144 (1918), 615-616. Anon., *Gas Age,* (1918), 548-50. Wattleworth, D. R., *Gas Wld.*, 69 (1918), 345. de Norman-lle, E., *Aero.*, 17 (1919), 164. *Pet. Age,* 6 (1919), 361. *J. S. A. E.*, 7 (1919), . Mackie, I. C., *Can. Chem. J.*, 3 (1919). Norcross, J. A., *Am. Gas Lt. J.*, ay 24, 1919, 433. Battle, J. R., *Nat. Pet. News,* Sept. 14, 1921, 30. Rathbun, B., *Pet. Mag.*, Jan., 1920, 150, 152, 154. Wehrmann, F., *Z. Elektrochem.*, 27 921), 397-8. Rile, W. M., *Pet. Mag.* 10 (1921), 129-131. Ellis & Meigs, bliography on Benzol as a Motor Fuel in "Gasoline" (1922), 541. Anon., *at. Pet. News,* July 26, 1922, 23. Halbert, W. K., *Nat. Pet. News,* Apr. 26, 22, 35.

Tetrahydronaphthalene.[18]

Tetrahydronaphthalene, or "tetraline" for short, is produced in Germany and used as a motor fuel,—usually in admixture with an equal volume of gasoline or benzol. "Tetraline" boils at 205° C., fuses at — 30° C., has a specific gravity of 0.9751, and a flash point of 78° C. It is made from naphthalene. So far as I can see there is little probability that tetraline will be of any consequence as a motor fuel in this country.

Naphthalene.[19]

Naphthalene is not suitable for use as a motor fuel because of its high melting point, and difficulty encountered in controlling the composition of the air-fuel mixture. However, the hydrocarbon may be dissolved in benzol or gasoline, and thus utilized. It is of small consequence in this country, but is used to some extent in Germany.

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Chapter XIV.

Gasoline Specifications and Quality.

The value of standards of quality has long been recognized in commerce. A definiteness is introduced into business relationships that lessens the number of disputes, and renders easier the settlement of differences that may and do arise. When agreements are made between two parties, the drawing of specifications that shall govern in the transactions is not ordinarily a matter of great difficulty. But the preparation of specifications that shall be used as a guide in the manufacturing and marketing activities of an industry of nation-wide scope is a problem of real difficulty. The petroleum industry in particular has always been reluctant to adopt hard and fast standards. The reason for this lies in the fact that the raw materials that form the basis of all operations are of great diversity. This is thoroughly appreciated and need not be discussed here.

Specifications must be so drawn that:

1. They result in the production of a better and more uniform product.

2. They do not discriminate against one manufacturer, or unduly favor another.

3. They do not restrict production and distribution unless such restriction is generally conceded to be desirable.

4. Simple and certain tests can be made to determine whether the product meets the specifications.

If the specifications are to stand scrutiny in the light of these conditions it is apparent that an exact analysis of the industry from an economic and technical standpoint must be made. The really essential facts must be known.

The outstanding economic fact of the oil industry of today is that there is a demand for every drop of gasoline that can be made. The outstanding technical fact is that the nature of the raw material and refinery technology both vary widely. Both of these facts indicate that in so far as the productive industry is concerned, latitude in specifications is not only desirable but necessary. But the consumer is entitled to equal consideration with the producer. From his standpoint several limitations are at least temporarily necessary.

What does the consumer require? Viewed solely from a technical standpoint he requires a fuel that will burn efficiently within the cylinders of an engine, that will not form troublesome gummy deposits in the carburetor, manifold pipes, or valve pockets, and that upon use

does not form products that will harm the engine either by direct contact in the cylinders or when dissolved in or mixed with the lubricating oil. Established marketing practices that may have little justification from a technical standpoint, but that are based on popular belief, are important in their effect on specifications. The public is not quickly educated to use products that do not conform to the standards to which it has been accustomed.

The factors that will or do require, or that have required, consideration in framing gasoline specifications, are briefly discussed in the following paragraphs.

Color.

The inclusion of a standard for color of gasoline is justified for two reasons. The more important of these is that it is easier to sell a gasoline of good color at retail. The layman has little or no knowledge of the properties that truly determine the value of a gasoline, and therefore turns to those properties that appear to him to be a reasonable basis for discrimination. Color and odor are the most obvious. In the second place a color standard demands care in refining, and in some measure prevents sloppy practices on the part of a careless or knowingly negligent refiner. Color as such cannot be regarded seriously from a purely technical standpoint, for a minute quantity of a dark colored oil mixed with a large quantity of gasoline will throw the product off-color. A tank or a tank-car that is not perfectly clean will easily discolor the gasoline therein, but it is hardly reasonable to suppose that the gasoline is thereby rendered a poorer fuel.

The specification for color may discriminate against the refiner of some types of benzines produced by cracking processes. It has been my experience, however, that these products can be treated in such a manner as to meet reasonable color requirements, and this without undue expense.

Odor.

There is less justification for the inclusion of a standard for odor in gasoline specifications than for one of color. Who shall say what the odor of gasoline shall be; and, of equal importance, how shall odor be measured? Odors become matters of habit. The sweetish odor of a properly refined cracked gasoline is offensive to some, but is pleasing to me. Recent specifications wisely say nothing of odor. The perspicacious refiner, however, will not fail to recognize that it is unwise to offend the esthetic sense of the buyer at retail, and will strive to make a product of at least reasonably good odor.

Water, Sediment, Foreign Matter.

Gasoline should not contain water, sediment, or foreign material. Ordinary care in production and distribution is all that is required to meet a specification to this effect.

Specific Gravity.

A few years ago the specific gravity of a gasoline was regarded as an important criterion of quality. The discovery of petroleums of new type, the use of cracking processes, and the manufacture of various blends introduced so many complicating factors that the gravity test has been dethroned and exiled. And rightly so, for a gasoline distilled from California petroleums with gravity of 53 to 54° Bé. may have a distillation range practically identical with that of a gasoline of 58 to 59° Bé. gravity made from Eastern crudes. The California gasoline is the better of the two on account of its chemical nature, but on the basis of a gravity test would be ranked much lower. Another class of gasolines that would be unjustly discriminated against if gravity tests were the basis of judgment are the cracked products, particularly those made by vapor-phase processes. The gravity of these may be 47 to 49° Bé., and yet the distillation range will be entirely satisfactory. The futility of gravity tests, and the injustices that attend their use, is now generally recognized.

Volatility.

The volatility of gasoline is the most important single characteristic. But the word volatility is somewhat misleading as it suggests that ease of vaporization, per se, is the only desirable and necessary property of a fuel that may be judged from measurement of volatility. On one hand it makes little difference if the fuel-air mixture enters the cylinders as a dry gas, or if part of it is in the form of minute droplets.[1] The combustion phenomena are not greatly different in the two cases. But combustion is only one part of the problem of utilization. Before the mixture can be burned it must be distributed through a manifold to the several cylinders. The difficulties of proper distribution are greater than is commonly supposed. Kettering and his collaborators have shown that a single cylinder engine can be operated economically when the air entering the carburetor is at a temperature of — 10° F. The engine operated satisfactorily at 15 pounds per sq. in. higher compression when the air entered at — 10° F. than when it entered at room temperature. These results are quite in contrast to those obtained with a multi-cylindered engine, and show the importance of uniform distribution of the fuel-air mixture to the several cylinders. A mixture containing droplets cannot be so uniformly distributed as a dry mixture because of force required to move the droplets, and because of the scrubbing action of the walls of the manifold.

The formation of the mixture is obviously dependent on the volatility of the fuel. Volatility in turn depends on the nature and relative amount of the substances contained in the heterogeneous mixture of hydrocarbons that is called gasoline. The nature of the hydrocarbons is now recognized as a matter of importance, for it is found that the troublesome and destructive knock that is now so common is charac-

[1] See Kettering, *J. Soc. A. Eng.*, 9 (1921), 296.

teristic of the combustion of some substances and not of others. Several papers [2] by Kettering and his coworkers should be consulted on this general subject. For example, kerosene, heavier oils, and ether knock badly when used as fuels in an automobile engine, but gasoline, ethyl alcohol, butyl alcohol, cyclo hexane, benzene, and carbon disulfide do not knock when used under similar conditions. Knocking is not dependent on preignition, for carbon disulfide when used as a fuel preignites but does not knock. Abnormal combustion, the occurrence of which is possibly the result of thermal dissociation of the fuel substances, is responsible for the knock. In the paraffin series the tendency to knock appears when the molecular weight of the fuel is above some point not yet definitely determined.[3] Since volatility and molecular weight are closely related in any particular series of hydrocarbons, the measurement of volatility will serve in some measure as a guide to the combustion characteristics of a hydrocarbon fuel of known source.

The commonly accepted test for volatility is the determination of the distillation range in accordance with the standard method of the Interdepartmental Petroleum Specifications Committee. The specification as written by this committee is the result of compromise between the conflicting opinions of many interested parties. The use of the distillation method for determining volatility has not gone unchallenged. For example R. E. Wilson [4] states that the distillation test is not a satisfactory criterion of volatility as related to ease of starting or to efficient distribution and combustion. His argument is based on the fact that vaporization in the distillation test does not simulate that in the carbureter. The former is progressive while the latter approaches a flash vaporization. I feel that there is much justification for Wilson's viewpoint. The entire matter must be studied with much care. It will first be necessary to show that the distillation test, and any other test that may be devised to supplant the distillation test, does in fact place different values on the fuels examined; and further, that the order of merit of the fuels is more truthfully shown by the new method of test than by the distillation test. In other words an analytical method that has served as long and as faithfully as the distillation test will not quickly give way to new methods. The burden of proof as to merit is with the newcomer.

Wilson has proposed a method for the determination of volatility that is correct in principle and deserves consideration. Howard [5] discusses the subject of volatility, and shows a cut of an apparatus designed by C. I. Robinson for the measurement of vapor pressure of gasoline. This apparatus, if used as stated in Howard's article, is open to the criticism that equilibrium is not established between the gaseous and

[2] C. F. Kettering, *J. S. A. E.*, 9 (1921), 291-6. *Motor Age*, Sept. 11, 1919, 20-1. *Nat. Pet. News*, Nov. 24, 1920, 55. T. Midgley, *Nat. Pet. News*, Jan. 12, 1921, 33. *Nat. Pet. News*, July 5, 1922, 59. *J. S. A. E.*, 10 (1922), 7.

[3] A study of these phenomena is being carried out under my direction in the Chemical Engineering Laboratories of the University of Michigan.

[4] *Bull. 203, Am. Pet. Inst.*, Dec. 30, 1921, 15-21.

[5] *J. S. A. E.*, 8 (1921), 145-8.

liquid phases. In general, dynamic methods of measuring the vapor pressure of gasoline will give incorrect results unless provision is made to establish equilibrium. Simple dynamic methods, such as Smith's "bubbly-bulblet," that are most satisfactory for measuring the vapor-pressure of pure liquids, are not at all applicable to gasoline because as vapor forms the composition of the liquid changes.

The vapor-pressure of various substances unless properly interpreted may lead to erroneous conclusions regarding the ease with which the substance could be used as a motor fuel. For instance, pentane is much more volatil than decane, but the ease with which satisfactory fuel mixtures could be prepared from these substances is more nearly represented by the products of vapor-pressure and the respective molecular weights. The chemical reactions of combustion are expressed in terms of weights, and it requires fewer molecules of decane than pentane to compose a gram or a pound of the substance. The lower vapor-pressure of decane is thus offset in some measure by its higher molecular weight.

The distillation test is now the standard method of gauging volatility. The choice of the temperatures at which 90 per cent of a gasoline shall distill, and that at which the flask shall be dry is often criticised. The discrepancy that exists is fully recognized by those who, in conference, were responsible for selecting these temperatures. The 90 per cent point is regarded as of more importance than the end-point since it is determined with more certainty. Any properly made gasoline that passes the 90 per cent specification is certain to pass the end-point specification. The converse is not true. A large number of gasolines that are now marketed will pass the end-point specification, but will fail to pass the 90 per cent specification. Within the last few years some refiners have greatly improved distillation technique. The result is that the upper part of the distillation curve of gasoline produced by them is more nearly a straight line. The average jobber or retailer pays more attention to end-point, than he does to the 90 per cent point, and as a consequence he buys kerosene in his gasoline.

Olefin Content.

Ten years ago the amount of gasoline produced by cracking processes was so small that the olefin content of gasoline did not need to be considered. Straight-run gasolines contain negligible quantities of olefins. The widespread use of cracking processes demands that the olefin content of gasolines receive more careful consideration. The vapor-phase processes in particular give products that may be most undesirable.

So far as current knowledge of the properties of olefinic gasolines may be relied upon in forming judgment, it can be said that the mono-olefins are not so undesirable as components of gasolines as to preclude the use of gasolines containing them. The reactions of these substances are discussed in greater detail in Chapter X on treating. Gasolines that

contain mono-olefins in amounts not greater than 10 to 15 per cent are apparently entirely satisfactory in use. Possibly a gasoline composed of 100 per cent mono-olefins would be satisfactory, but it has been noted that those gasolines that contain over 20 per cent of olefins are frequently found to cause trouble by the formation of gummy deposits on the valve-stems, valve-pockets, and sometimes in the carburetor. These difficulties are probably caused not by the mono-olefins, but by easily oxidized and polymerized di-olefins. A benzine that caused the formation of extensive gummy deposits within four hours time in a Maxwell engine was used with entire satisfaction after it had been refined with a few pounds of sulfuric acid per barrel, washed with dilute caustic soda solution, and steam-distilled.

One difficulty in framing specifications to cover the olefin content of gasolines lies in the lack of suitable analytical methods for determining the percentage of these compounds in the product. At present there is no quantitative method for determining olefins. Possibly such a method is not required, but one is needed that will measure the content of undesirable olefin components.

Until our knowledge of the chemistry of the olefins and of their value as engine fuels is much more extensive than at present it will be unwise to draw rigid specifications covering the allowable content of these compounds in gasoline.

Gum Forming Components.

The formation of gummy deposits has already been referred to in the previous section. The tests now used can hardly be considered a satisfactory basis for the establishment of definite specifications. Before these can be drawn, the nature and cause of gummy deposits must be carefully studied.

Some engineers consider that gum formation outside the cylinders and carbon formation within the cylinders are attributable to the same components of the gasoline. Others believe that carbon formation is the result of imperfect combustion, of decomposition of the lubricating oil or both. I am inclined to the latter view as I believe the oxidative phenomena of combustion to be concurrent with thermal dissociation of the hydrocarbons. In processes of thermal dissociation at temperatures such as those within the cylinder there must be at least moderate formation of di-olefin compounds. I see no reason, therefore, to condemn gasolines that contain small quantities of the di-olefins if such condemnation is based on the formation of carbon within the engine cylinder.

Gum forming components cause trouble when gasoline is stored. Sticky deposits are formed in the tanks, and the gasoline may develop a sharp and unpleasant odor. N. A. C. Smith and M. B. Cooke[5a] have conducted important experimental work designed to ascertain the nature of gums and the reasons for their formation. They find that

[5a] Ser. No. 2394, U. S. Bur. Min., Sept., 1922.

oxidation is the most important factor involved in the formation of these substances, but that the water and light both aid in the process, although they are not essential to it. No direct relationship between unsaturation and gum formation was found, and the analytical method for unsaturation is not an index of gum formation. The experiments of Smith and Cooke indicate that gums are produced by a process of oxidation of olefins to aldehydes, followed by polymerization of the aldehydes. The method used by these investigators to determine "gum" in gasoline is given in Chapter XVI. The serial publication describing their experiments is easily obtainable and should be consulted for a detailed description of their work.

Sulfur Compounds.

The notorious reputation of sulfur as an impurity in steels, as a poisoner of catalysts, as a cause of bad odors, and in many other connections has led many to the unquestioned belief that it is harmful as a component of fuel for explosion engines. Unless the sulfur is in combination in such a form that it will combine with the metals from which the carburetor is constructed it is difficult to see how small to moderate amounts of sulfur can do harm in a motor fuel. Sulfur dioxide and possibly small amounts of sulfur trioxide are formed when sulfur burns. These gases are harmful to metals when dissolved in water to form sulfurous and sulfuric acids. But the formation of liquid water is out of the question in the cylinder or exhaust manifold. If the pistons are leaky, water vapor along with small amounts of these gases might escape into the crank case. Even so, it is difficult to believe that serious harm would be done to the oil covered metal parts, although the possibility of harm must be admitted.

Another possibility is that of direct action of metals on the SO_2 or SO_3 present in the products of combustion. This has been the subject of study by E. B. Tucker and S. E. Ullman working under my direction at the University of Michigan. Their experiments showed that when the proportion of SO_2 was no greater than 0.000085 per cent by volume in flue gases at 500° C. combination of the sulfur of the SO_2 with iron to form a sulfide occurred. Carbon steel was more affected than nickel steel, and gray cast-iron was scarcely affected at all. The extent of the reaction was judged by taking sulfur prints. None of the metal specimens used showed sulfur prints after being heated in blank tests. A gasoline containing 0.035 per cent sulfur (equivalent to 0.00171 per cent SO_2 in the combustion gases) caused a marked formation of sulfides. While these experiments demonstrate that sulfur dioxide is reduced by iron at 500° C., they do not prove that serious damage would be done by a fuel containing a few hundredths of 1 per cent of sulfur. It seems hardly reasonable to me that the relatively heavy cast-iron walls of the cylinders or exhaust manifold would be seriously affected within the life of the average motor-car. The possibility of damage, however, cannot be denied.

C. K. Francis[6] in an article on "Sulfur in Gasoline" states that properly refined gasoline should contain less than 0.01 per cent sulfur, but that gasolines containing up to 0.04 per cent sulfur might be acceptable. The harmful effect is evidenced in the corrosion of copper and brass tubing and connections, and of the cylinder surfaces. Sulfur is contained in the deposits commonly called "Carbon." According to Francis the deleterious effect of sulfur is noticed when 0.008 per cent is present, and a serious corrosive action is observed when 0.018 per cent is present. The sulfur content of Mid-Continent gasolines is ordinarily between 0.01 per cent and 0.05 per cent.

It is my opinion that the evidence at hand is insufficient to allow of the drawing of definite conclusions as to the effect of sulfur. Until such evidence is available it will be wise to include the copper corrosion test, now a part of the Motor Gasoline specification written by the Interdepartmental Petroleum Specifications Committee.

Acidity.

The acidity of gasoline may be caused by inorganic or organic acids. There is no excuse for refining gasoline in such a manner that inorganic acids are contained in the product. Some difficulty may be encountered in avoiding the formation of SO_2 in the steam-distillation of treated gasoline made by vapor-phase cracking.

Little attention is paid to organic acidity. It is apparently assumed that the quantity of organic acids present in gasolines is too small to be harmful. Probably this is true, but it is by no means proved.

"Vapor-pressure."

The pressure exerted by gasoline when a definite volume is confined in a definite space at a specified temperature is referred to as the "vapor-pressure." I use the quotation marks since the property measured in this way is not the vapor-pressure. The determination of the pressure is of value in judging whether the product can be shipped with safety in a tank-car. The determination of the "vapor-pressure" as specified by the Interstate Commerce Commission[7] is given in Chapter XVI. The method is not satisfactory, and will undoubtedly be revised soon.[8]

Gasoline shall not be shipped in tank-cars if the "vapor-pressure" at 100° F. is greater than 10 lbs. per sq. in. If the "vapor-pressure" is between 10 and 15 lbs. per sq. in. (between April 1 and Oct. 1) or between 10 and 20 lbs. per sq. in. (Oct. 1 to April 1) the product must be shipped in metal drums complying with Shipping Container Specifications No. 5, or in special insulated tank-cars approved for this service by the Master Car Builders' Association.

[6] *Chem. Met. Eng.*, 23 (1920), 291-3.

[7] Pub. Bur. Expl., 30 Vesey St., N. Y. C. B. E. Pamph. 9, and supplements thereto.

[8] See "Hazards Involved in the Transportation of Natural-Gas Gasoline," by D. B. Dow. Pub. U. S. Bur. Min. in coöperation with the Assoc. Nat. Gas. Mfrs., Jan., 1922.

If the "vapor pressure" is above 15 or 20 lbs. as provided above, and not in excess of 25 lbs., the product must be shipped in metal drums complying with Shipping Container Specification No. 5.

If the "vapor-pressure" exceeds 25 pounds metal cylinders must be used as containers.

While these clauses are not ordinarily written into specifications for gasoline the shipment of the product must conform to these rules and regulations.

Specifications of the Interdepartmental Petroleum Specifications Committee.

The specifications of this committee have been officially adopted by the Federal Specifications Board for the use of the various departments and independent establishments of the Government. They supersede the specifications published in Bulletins 1-5 inclusive, of the Committee on Standardization of Petroleum Specifications. For details of authority, personnel, and specifications on petroleum products other than gasolines, reference should be made to Technical Paper 305, U. S. Bureau of Mines, published in 1922. The methods to which reference is made are those given in Tech. Paper 298 of the U. S. Bureau of Mines.

Specifications for Gasoline.

Aviation Gasoline, Fighting Grade.

General Statement.

1. This specification covers the grade of gasoline used by the United States Government and its agencies, as a fuel for fighting planes where the highest efficiency is required.

2. The gasoline shall be free from undissolved water and suspended matter.

Properties and Tests.

3. *Color.*—Method 10.1. The color shall not be darker than No. 25 Saybolt.

4. *Doctor Test.*—Method 520.3. The doctor test shall be negative.

5. *Corrosion Test.*—Method 530.1. One hundred cc. of the gasoline shall cause no gray or black corrosion and no weighable amount of deposit when evaporated in a polished copper dish.

6. *Unsaturated Hydrocarbons.*—Method 550.1. Not more than 1 per cent of the gasoline shall be soluble in concentrated sulphuric acid.

7. *Distillation Range.*—Method 100.1. The temperature limits for the distillation are as follows:

When 5 per cent of the sample has been recovered in the graduated receiver, the thermometer shall not read more than 65° C. (149° F.) or less than 50° C. (122° F.).

When 50 per cent has been recovered in the receiver, the thermometer shall not read more than 95° C. (203° F.).

When 90 per cent has been recovered in the receiver, the thermometer shall not read more than 125° C. (257° F.).

When 96 per cent has been recovered in the receiver, the thermometer shall not read more than 150° C. (302° F.).

The end point shall not be higher than 165° C. (329° F.).

At least 96 per cent shall be recovered as distillate in the receiver from the distillation.

The distillation loss shall not exceed 2 per cent when the residue in the flask is cooled and added to the distillate in the receiver.

8. *Acidity.*—Method 510.2. The residue remaining in the flask after the distillation is completed shall not show an acid reaction.

9. The United States War Department required the fighting grade to be colored red after inspection and acceptance.

10. All tests shall be made according to the methods for testing petroleum products adopted by the Interdepartmental Petroleum Specifications Committee. (See Technical Paper 298, Bureau of Mines.)

Aviation Gasoline, Domestic Grade.

General Statement.

1. This specification covers the grade of gasoline used by the United States Government and its agencies for aviation fuel where the fighting grade is not required.

2. The gasoline shall be free from undissolved water and suspended matter.

Properties and Tests.

3. *Color.*—Method 10.1. The color shall not be darker than No. 25 Saybolt.

4. *Doctor Test.*—Method 520.3. The doctor test shall be negative.

5. *Corrosion Test.*—Method 530.1. (Specification modified Oct. 31, 1922, to read as here given.) One hundred cc. of the gasoline shall cause no gray or black corrosion, and the weighable amount of deposit when evaporated in a polished dish shall not exceed 3 milligrams.

6. *Unsaturated Hydrocarbons.*—Method 550.1. (Specification modified Oct. 31, 1922, to read as here given.) If the gasoline is to be stored for more than 90 days from the date of delivery, not more than 2 per cent of the gasoline shall be soluble in concentrated sulfuric acid.

7. *Distillation Range.*—Method 100.1. The temperature limits are as follows:

When 5 per cent of the sample has been recovered in the graduated receiver, the thermometer shall not read more than 75° C. (167° F.), or less than 50° C. (122° F.).

When 50 per cent has been recovered in the receiver, the thermometer shall not read more than 105° C. (221° F.).

When 90 per cent has been recovered in the receiver, the thermometer shall not read more than 155° C. (311° F.).

When 96 per cent has been recovered in the receiver, the thermometer shall not read more than 175° C. (347° F.).

The end point shall not be higher than 190° C. (374° F.).

At least 96 per cent shall be recovered as distillate in the receiver from the distillation.

The distillation loss shall not exceed 2 per cent when the residue in the flask is cooled and added to the distillate in the receiver.

8. *Acidity.*—Method 510.2. The residue remaining in the flask after the distillation is completed shall not show an acid reaction.

9. All tests shall be made according to the methods for testing petroleum products adopted by the Interdepartmental Petroleum Specifications Committee. (See Technical Paper 298, Bureau of Mines.)

Aviation Gasoline, Benzol Blended.

This specification has been withdrawn, as further work on it is contemplated.

Motor Gasoline.[8a]

General Statement.

1. This specification covers the grade of gasoline used by the United States Government and its agencies as a fuel for automobile, motor boat, and similar engines.

Properties and Tests.

2. *Color.*—Method 10.1. The color shall not be darker than No. 16 Saybolt.

3. *Corrosion Test.*—Method 530.2. A clean copper strip shall not be discolored when submerged in the gasoline for 3 hours at 122° F.

4. *Distillation Range.*—Method 100.1. When the first drop has been recovered in the graduated receiver, the thermometer shall not read more than 55° C. (131° F.).

When 20 per cent has been recovered in the receiver, the thermometer shall not read more than 105° C. (221° F.).

When 50 per cent has been recovered in the receiver, the thermometer shall not read more than 140° C. (284° F.).

When 90 per cent has been recovered in the receiver, the thermometer shall not read more than 200° C. (392° F.).

The end point shall not be higher than 225° C. (437° F.).

At least 95 per cent shall be recovered as distillate in the receiver from the distillation.

5. All tests shall be made according to the methods for testing

[8a] The specification here given includes the revision adopted by the Interdepartmental Petroleum Specifications Committee on October 31, 1922.

petroleum products adopted by the Interdepartmental Petroleum Specifications Committee. (See Technical Paper 298, Bureau of Mines.)

Other Grades of Gasoline.

In addition to the several grades of gasoline covered by the official specifications given above, several other products are marketed. Among these may be mentioned:

Cymogene. This is the lightest distillate obtained from petroleum. It consists largely of butane, boils about 32° F. and has a Baumé gravity of 90 to 110. Its use is very limited.

Rhigolene. This consists largely of pentane, boils about 65° F. and ranges in gravity from 90 to 100° Bé.

Solvent Gasoline. If made from Pennsylvania crude, this ranges in gravity from 72 to 76° Bé. and if made from Mid-Continent crude, 68 to 70° Bé. It may have an initial boiling point of 100 to 120° F. and an end point of 275 to 300° F. This product has a limited use as a very volatil fuel, but is mainly used as a solvent in extraction processes or for dissolving rubber, resins, and gums.

Cleaners' Gasoline. This is somewhat heavier than solvent gasoline and in general is similar to the product that was formerly sold so widely as standard automobile gasoline. In general it approaches to the government specifications for aviation gasoline. It finds use as a fuel in air-gas machines, safety lamps, soldering torches, and as cleaner's naphtha.

Motor Gasoline. The standard specification for motor gasoline has been given. It is not true, however, that all motor gasolines marketed in this country conform to this specification. Numerous grades are sold ranging in volatility from that of aviation gasoline, usually sold under some such designation as "high test," to a product with an end point of 450-460° F.

State Specifications.

The desirability of uniformity in State Specifications for gasoline needs no argument. It would appear that the several States could do no better than to adopt the specifications of the Interdepartmental Petroleum Specifications Committee. The present laws of the States show great diversity, and in some cases are obviously ill-advised. They are given below for convenient reference.

State Gasoline Inspection and Tax Laws.

Alabama.

The distillation test shall show an initial boiling point of 140° F., 18 per cent at 250° F. or below, and an end-point below 437° F. Tax on gasoline is 1/20 cent per gallon.

Arizona.

No specification, but levies a road tax of 1 cent per gallon.

Arkansas.

The gravity shall be taken at 60° F. and marked on the container. Road tax of 1 cent per gallon, and inspection tax of 1/8 cent per gallon.

California.

No law and no tax. Los Angeles has adopted a motor transport specification.

Colorado.

Gravity shall be taken. No gasoline shall be offered for sale that contains over 5 per cent of solid matter. Road tax of 1 cent per gallon.

Connecticut.

No law. Road tax of 1 cent per gallon.

Delaware.

No law and no tax.

Florida.

Gravity shall be placed on label. Road tax of 1 cent per gallon and inspection tax of 1/8 cent per gallon.

Georgia.

Gravity shall be taken and no product known as gasoline, benzine or naphtha shall be offered for sale unless casks, barrels, or packages containing such products are labeled with figures denoting gravity and the words "gasoline," "Benzine" or "naphtha," in large red letters. Road tax of 1 cent per gallon. General tax of 1/2 cent per gallon for inspection.

Idaho.

The standard adopted by the U. S. Bureau of Mines shall be standard. Must be labeled and sold under true name.

Illinois.

Must be labeled "Condemned for illuminating purposes." No tax.

Indiana.

Gravity shall not be less than 56° Bé. The correction of gravity for temperature shall be 1° Bé. for each 10° F.

Iowa.

Gravity shall be between 80° Bé. and 70° Bé. Boiling point shall not be below 150° F. and not above 210° F. All other products shall be branded "Substitute for gasoline," and these substitutes shall be sold under label, which label shall be printed in large, legible type, etc., defined as follows:

(a) Per cent of, boiling below 135° F.
(b) Per cent of, boiling between 135° F. and 210° F.
(c) Per cent of, boiling between 201° F. and 302° F.
(d) Per cent boiling above 302° F.

Bills of lading and the labels of such substitutes shall call attention to the danger of such low boiling point. No tax.

Kansas.

Shall be water-white, sweet by the doctor test, and shall contain no acid. Gravity test is required. 20 per cent shall distill below 230° F., 50 per cent below 325° F., and end-point shall not be above 450° F. Tax is levied.

Kentucky.

No laws. Road tax of 1 cent is levied.

Louisiana.

No law. Road tax of 1 cent is levied.

Maine.

Must be labeled "unsafe for illuminating purposes."

Maryland.

No law.

Massachusetts.

No law.

Michigan.

Gasoline must be correctly labeled. Grand Rapids, 20 per cent shall distill over, at, or below 320° F. 50 per cent shall distill over, at, or below 300° F. End-point not above 450° F. If product does not meet this test, it shall be known as a mixed gasoline-kerosene; Detroit, same law as Grand Rapids, but method of distillation is entirely different. Gasoline passing Grand Rapids specification by their method of distillation, might be rejected by Detroit.

Minnesota.

Initial b.p. not over 140° F., 20 per cent over at 221° F., 50 per cent at 315° F., 90 per cent at 420° F., and end-point not over 450° F. The residue shall not be over 3 per cent in the distillation and 86 per cent at least shall be recovered. Gasoline must be labeled "Unsafe for illuminating purposes." The results of test shall be placed on label. Any gasoline marked "high-test" shall be a superior product.

Mississippi.

No laws.

Missouri.

Products sold as gasoline must be over 58° Bé. Products of 50 to 58° Bé. gravity shall be sold as mixed gasoline or naphtha.

Montana.

Must be free from water, acid, and foreign matter, and shall be de-odorized. Initial b.p. not over 140° F., 20 per cent between 158°

and 221° F., 50 per cent below 275° F., 90 per cent below 390° F., and end-point below 460° F. The product is acceptable if sum of 20 per cent and 90 per cent temperatures is less than 611.

Nebraska.

New Navy specification. Shall contain no water, or impurities, and shall be water-white.

Nevada.

No laws.

New Hampshire.

No law.

New Jersey.

The product shall be properly labeled.

New Mexico.

The gravity shall be over 46° Bé. Road tax of 1 cent per gallon.

New York.

No law.

North Carolina.

New Navy distillation range. Loss in distillation to be not over 5 per cent. Notice of shipment with full information must be sent by the manufacturer to the Commissioner of Agriculture, Raleigh, N. C. Road tax of 1 cent, and inspection tax of 1/4 cent per gallon.

North Dakota.

Class I. or household gasoline shall not show less than 3 per cent distilled at 158° F., and not over 6 per cent residue at 284° F. Class I. product is not taxed. Class II. gasoline shall show 3 to 15 per cent distilled below 158° F., not over 36 per cent residue in flask at 284° F., and end-point not over 428° F. At least 96 per cent shall be recovered in the distillation. A tax of 1/4 cent per gallon is levied on this gasoline. Class III. comprises all other gasolines and is taxed 1 cent per gallon.

Ohio.

Gasoline shall be labeled "Dangerous."

Oklahoma.

High-grade or aero gasoline shall be water-white and free from acid. 5 per cent shall distill below 122° F. and 97 per cent below 350° F. All other gasoline shall be labeled "Motor fuel oil" and the quality stated.

Oregon.

Gravity shall not be less than 56° Bé. Road tax of 2 cents per gallon.

Pennsylvania.

Road tax of 1 cent per gallon.

Rhode Island.

No law.

South Carolina.

New Navy Specifications. Inspection tax of 1/8 cent per gallon.

South Dakota.

Gas machine gasoline, light gasoline, power gasoline, when made from Mid-Continent crude shall be as follows: Gas machine gasoline, not less than 64° Bé.; residue not more than 4 per cent. at 300° F.; all off below 350° F. Light gasoline, gravity not less than 60° Bé.; residue not over 10 per cent above 300° F. and not more than 25 per cent above 350° F. Power gasoline, gravity not less than 57° Bé.; residue not more than 25 per cent at 300° F. and not more than 3 per cent at 400° F. Below is a table giving gravities depending upon what crude the products are made from:

	Gravity in degrees, Bé.	
	Mid-Continent Field	Pennsylvania Field
Gasoline for use in automobile engines and in other gasoline engines should have a gravity of not less than	57	62
Gasoline for household use in stoves, flatirons, gasoline lamps, dry cleaning, etc., should have a gravity of not less than	62	65
Gasoline for use in gas machines for the production of gasoline gas, should have a gravity of not less than	70	80
Naphtha for use in engines, and for other purposes should have a gravity of not less than	55	..

In describing kerosene or gasoline by its gravity it is necessary to indicate the State or Territory producing the crude petroleum from which the finished product was distilled, because crude petroleum differs in different regions and its products differ likewise. In stating the crude petroleum fields above, the Mid-Western is taken to include Texas, Oklahoma, Kansas, Wyoming, Illinois and other oil-producing states in the West-central portion of the United States. The Pennsylvania field includes Pennsylvania, West Virginia and neighboring states.

Tennessee.

The container shall be branded "Gravity not less than ——° Bé., unsafe for illuminating purposes; for power purposes only."

Texas.

Initial 140° F., 20 per cent shall distill below 221° F., 45 per c below 275° F., 90 per cent below 356° F., and end-point shall be 4 F. or less. 95 per cent shall be recovered in the distillation. Va pressure shall be less than 10 pounds at 100° F.

Utah.

Must be properly labeled. U. S. Bureau of Mines Specifica shall be the Standard in Salt Lake City.

Vermont.

No law.

Virginia.

No law.

Washington.

Containers shall be labeled with the gravity. Road tax 1 cent gallon.

West Virginia.

No law.

Wisconsin.

Containers shall be labeled with the gravity. Inspection tax 5 c per barrel.

Wyoming.

New Navy Specification. Not over 2 per cent unsaturated hyc carbons.

The Quality of Gasoline Marketed in the United States.

The U. S. Bureau of Mines has taken upon itself the task of m ing semi-annual reports on the quality of gasoline marketed in United States. This is a most creditable and useful service, and i hoped that the Bureau will be able to continue the good work. first report of this character was written by Rittman, Jacobs, and D and entitled the "Physical and Chemical Properties of Gasolines S Throughout the United States During the Calendar Year 1915." [9] 1920, *Bulletin 191* of the U. S. Bureau of Mines, written by H. H. and E. W. Dean, and entitled "Quality of Gasoline Marketed in United States," was published. This bulletin contains the results the gasoline quality surveys of 1917 and 1919 along with much o useful information on the production and consumption of gasol Since January of 1920 semi-annual surveys of the quality of ma gasoline have been made.[10]

[9] U. S. Bur. Min., Tech. Paper 163, 1916.

[10] Ser. 2220, "Third Semi-Annual Motor Gasoline Survey," Feb., 1921. 2272, "Fourth Semi-Annual Motor Gasoline Survey," Aug., 1921. Ser.

Samples of gasoline from New York City, Washington, Pittsburgh, Chicago, New Orleans, St. Louis, Denver, Salt Lake City, and San Francisco are collected and analyzed. In the survey of July, 1922, a total of 132 samples were examined.

In each two-year interval between 1915-1917, and 1917-1919, a marked decrease in volatility of gasoline occurred. The changes since January, 1920, have not been great, as can be seen from an inspection of Table LXXVI. A somewhat closer study of the data than is possible from a summarized table shows that quality was lower in July, 1920, than in January of that year, but that an improvement was shown between July, 1920, and January, 1921.

TABLE LXXVI

AVERAGE RESULTS OF U. S. BUREAU OF MINES MOTOR GASOLINE SURVEYS

	Federal Specification	Jan., 1920	July, 1920	Jan., 1921	July, 1921	Jan., 1922	July, 1922
Spec. Grav.	....	0.746	0.747	0.745	0.747	0.745	0.752
Baumé or A. P. I. Degree*	....	57.8	57.5	58.0	57.5	58.0	56.8
Initial B. P.	140 (131° F. after Oct. 31, 1922)	113	124	102	125	102	121
20%	221	196	200	199	202	200	208
50%	284	260	260	266	262	267	270
90%	374 (392° F. after Oct. 31, 1922)	377	375	377	377	377	375
Final B. P.	437	429	430	430	433	430	429
Average B. P.	....	263	268	267	270	268	273
% Recovered	95.0	95.8	96.7	95.9	96.7	96.0	96.8

*The figures for July, 1920, to Jan., 1922, inclusive, are Baumé degrees, but for July, 1922, A. P. I. degrees.

A comparison of the motor gasoline survey of July, 1921, and July, 1922, in the several cities is given in Table LXXVII.

"Fifth Semi-Annual Motor Gasoline Survey," Feb., 1922. See also Ser. 2342, "Survey of Pacific Coast Petroleum Products," April, 1922. Ser. 2388, "Sixth Semi-Annual Motor Gasoline Survey," August, 1922.

TABLE LXXVII

COMPARISON OF MOTOR GASOLINE SURVEYS IN SEVERAL CITIES

JULY, 1921 AND JULY, 1922

District	Date	First Drop	20%	50%	90%	End-Point	Average B. P.
New York	July, 1921	125	208	265	365	422	268
	July, 1922	120	208	268	362	420	269
Difference		−5	Same	+3	−3	−2	+1
Washington	July, 1921	130	204	263	387	442	274
	July, 1922	121	200	258	370	426	266
Difference		−9	−4	−5	−17	−16	−8
Pittsburgh	July, 1921	112	181	247	382	435	259
	July, 1922	117	189	256	375	429	263
Difference		+5	+8	+9	−7	−6	+4
Chicago	July, 1921	125	202	261	389	444	273
	July, 1922	120	207	272	386	436	276
Difference		−5	+5	+11	−3	−8	+3
New Orleans	July, 1921	131	214	279	376	427	279
	July, 1922	141	219	275	373	427	279
Difference		+10	+5	−4	−3	Same	Same
St. Louis	July, 1921	128	205	268	383	441	276
	July, 1922	116	206	278	392	443	280
Difference		−12	+1	+10	+9	+2	+4
Denver	July, 1921	133	213	275	399	458	286
	July, 1922	118	224	288	385	437	285
Difference		−15	+11	+13	−14	−21	−1
Salt Lake City	July, 1921	126	200	256	353	401	259
	July, 1922	113	200	262	361	412	263
Difference		−13	Same	+6	+8	+11	+4
San Francisco	July, 1921	129	206	258	356	421	265
	July, 1922	123	214	268	370	430	273
Difference		−6	+8	+10	+14	+9	+8
9 Districts	July, 1921	125	202	262	377	433	270
	July, 1922	121	208	270	375	429	273
Difference		−4	+6	+8	−2	−4	+3
Federal specifications	Nov. 25, 1919	140	221	284	374	437	

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Chapter XV.

Distillation in the Laboratory.

The extensive use of distillation as a laboratory procedure renders essential a brief discussion of laboratory distillation apparatus. Analytical procedures are not to be considered here, but are presented in Chapter XVI.

Distillation in the laboratory may be conducted either to separate mixtures of substances into their components as nearly as is possible, or it may be conducted for purposes that do not require separation of the mixture. An example of the latter operation is the separation of water from either heavy oils or tars. The distillation operation is really one of dehydration. The liquid phase is an emulsion and not a solution. An apparatus that can be used for the second type of distillation is that of Allen and Jacobs.[1]

Distillations conducted for the purpose of effecting separations may be either of two limiting types: (1) distillation in which a moderate degree of separation is required, (2) distillation in which the separation should be as complete as possible. The standard laboratory distillation of gasoline is an example of the first type. This distillation is therefore conducted in an Engler type flask. This apparatus, because it offers only a limited cooling surface, because it tends to function at a temperature controlled by the temperature of the air surrounding the flask rather than by the composition of liquid and vapor, and because the vapor in its short passage from the flask to the delivery tube is not brought into intimate contact with liquid returning to the flask, is an ineffective means for effecting separation. If no condensation occurred in the flask or in the neck, the Engler flask would produce essentially the separation effected by one "perfect column-section." The subject matter of Chapter IV should be recalled in this connection.

The chemist in the petroleum laboratory has not frequently been concerned with methods and apparatus that would produce effective separations of substances by distillation. The stills used in the refinery did not effect clean separations, and it therefore seemed unnecessary greatly to better plant results in the laboratory. However, the development of refinery methods that allow effective separation has necessitated the use of better apparatus in the laboratory.

Other industries, in which the distillation of liquid mixtures is an important part of manufacturing operations, have long used better

[1] U. S. Bur. Min., *Bull. 19*, "Physical and Chemical Properties of the Petroleums of the San Joaquin Valley in California."

methods, both in the plant and in the laboratory, than the oil industry.

In the paragraphs that follow, I shall describe a number of apparatus that have been used for laboratory distillation. I wish to make it perfectly clear, however, that I do not subscribe to the proposition that these apparatus are necessarily effective in operation. It would be a waste of time and space to give a detailed description of each apparatus. The reason for this lies in the fact that our present knowledge of the subject of distillation is so far beyond that existent when most of these apparatus were designed, that they are interesting mainly from an historical standpoint. The principles that should govern the design of laboratory distillation apparatus are exactly the same as those outlined in Chapter IV. The most effective and most efficient apparatus will be the one that brings the countercurrently flowing liquid and vapor phases into intimate contact, and that condenses and returns to the top of the contacting column the proper amount of reflux at all times during the distillation. A casual examination of many of the older types of laboratory distillation apparatus is sufficient to show how imperfectly these objectives are accomplished.

At this point it should also be recalled from Chapter IV that differential dephlegmation is a process that can be made the basis of effective and fairly efficient separations of liquid solutions. Differential dephlegmation is never as efficient as distillation through a contacting column. It will be recalled that in order to have true differential dephlegmation, the liquid condensed in the still-head should be removed as soon as it forms. This operation, therefore, requires a distinctly different type of apparatus than a column. It is interesting to note that this distinction has not been made in the design of many laboratory still-heads. A number of these apparatus are peculiar combinations of apparent attempts to attain differential dephlegmation and countercurrent contacting at the same time. As I have already stated, I do not care to enter into a detailed discussion of each apparatus in the light of these principles. At the conclusion of my description of the various types of apparatus, I shall present an apparatus which is designed correctly, and which has been found to be very effective in laboratory work. Quantitative separations of binary mixtures of many liquids are effected by a single distillation in this apparatus.

A Review of Laboratory Distillation Apparatus.

Probably the earliest comparison of laboratory still-heads was made by Kreis[2] who concluded that the Linnemann and Hempel heads were superior to the Wurtz bulb for the fractionation of volatil liquids.

Young[3] studied and compared the plain tube, the Rod and Disc, the Wurtz, the Pear, the "Evaporator," the Hempel, the Linnemann, the Glinsky, the LeBel-Henninger, and the Young and Thomas still-heads, or "dephlegmators" as he pleases to call some of them. These

[2] *Ann.*, 224 (1884), 259-69.
[3] "Fractional Distillation," 158-79. Thorpe's Dict. App. Chem., 271-3.

as well as other heads are shown in Figures 135 and 136. Comparative data are shown in Table LXXVIII.[4]

TABLE LXXVIII

YOUNG'S COMPARATIVE DATA ON STILL-HEADS *

Nature of Still-head or Dephlegmator	Plain vertical, 5.1 mm. diameter	Plain vertical, 14.0 mm. diameter	Plain vertical, 25.7 mm. diameter	"Rod and disc," 14 mm. diameter	"Pear"	"Evaporator"	"Evaporator"	"Evaporator"	"Hempel" with 200 beads	Glinsky	Le Bel-Henninger	Young and Thomas	Young and Thomas
Number of discs, bulbs, or sections	....	....	....	20	13	3	5	8	....	3	3	3	18
Vertical height in cm.	62	62	62	62	62	46	62	78	58	30	43	51	130
Final Temperature of Fraction	Percentage Weight of Distillate												
83.2	....	....	....	1.4	3.0	12.80	26.00	35.85	20.6	1.1	0.5	0.6	38.8
86.2	0.5	0.1	0.2	18.1	26.2	21.15	12.35	6.50	15.4	11.7	17.8	21.8	4.1
89.2	22.2	12.8	20.0	15.8	11.0	7.50	5.60	2.90	7.2	17.3	15.9	14.3	1.9
92.3	16.5	21.5	18.8	9.7	5.8	4.80	3.25	2.15	3.4	11.9	8.8	7.8	1.8
95.4	9.2	11.0	9.2	6.1	5.2	3.35	1.95	1.40	3.2	7.5	7.2	5.0	1.3
98.5	7.2	8.9	7.2	4.2	2.4	2.70	1.30	1.15	2.2	5.6	4.3	4.7	1.2
101.6	5.8	7.4	4.7	3.8	2.4	2.30	1.80	1.05	1.8	5.7	4.8	4.0	0.9
104.6	5.5	6.2	5.9	4.2	2.8	2.50	1.50	1.15	2.9	5.6	4.6	3.6	1.2
107.6	5.9	7.3	6.4	4.3	3.6	3.50	2.45	1.60	3.2	8.9	5.5	5.2	2.0
110.0	7.1	8.4	10.0	8.0	5.0	6.50	4.20	3.95	6.8	13.7	9.8	7.3	4.0
110.6	8.9	9.0	7.2	6.6	11.0	10.50	11.40	9.60	8.4	2.5	6.8	9.8	8.1
Pure toluene by difference	11.2	7.4	10.4	17.8	21.6	22.40	27.90	32.70	24.9	8.5	14.0	15.9	34.7
Weight of liquid and vapor in still-head	1.05	1.55	3.15	2.35	2.6	2.70	4.55	6.25	7.85	2.8	5.85	2.8	12.1

* From Thorpe's Dictionary, Vol. II.

The data of Table LXXVIII were obtained by distilling 50 cc. of a mixture of benzene and toluene at a rate of one drop per second. Young speaks of the "efficiency" of the various still-heads although his distillation procedure would in no way indicate efficiency. Hence in reviewing his results, the word "effectiveness" will be used in the sense

[4] Thorpe's Dictionary, Vol. II.

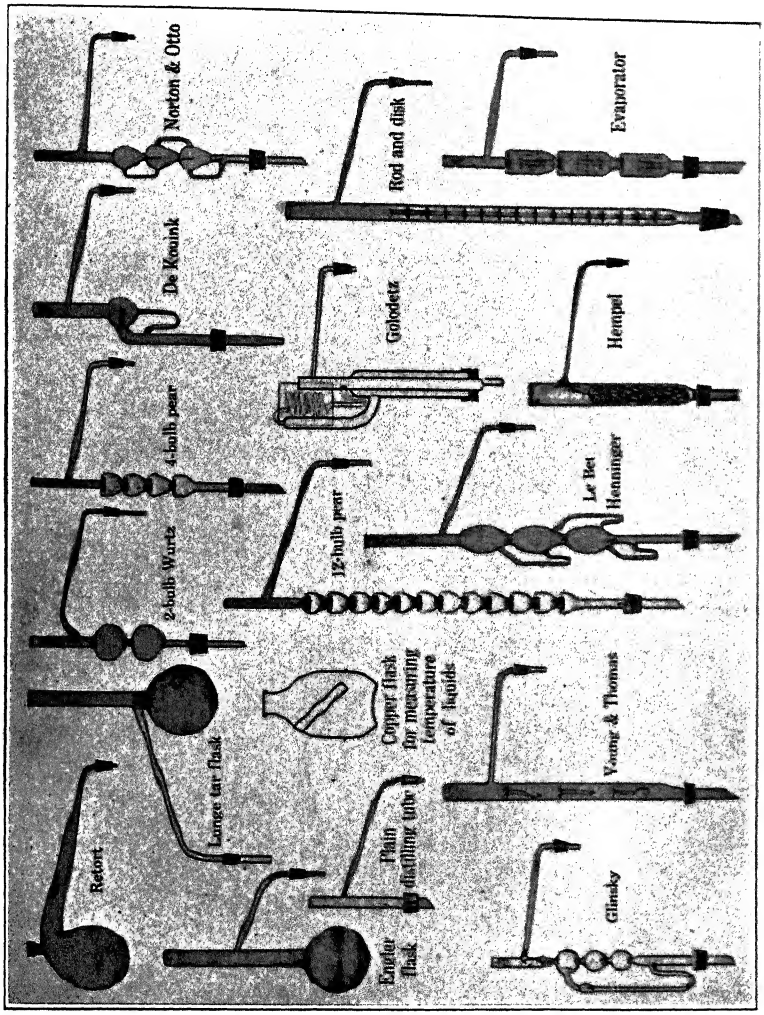


FIG. 135.—Laboratory Still-Heads.

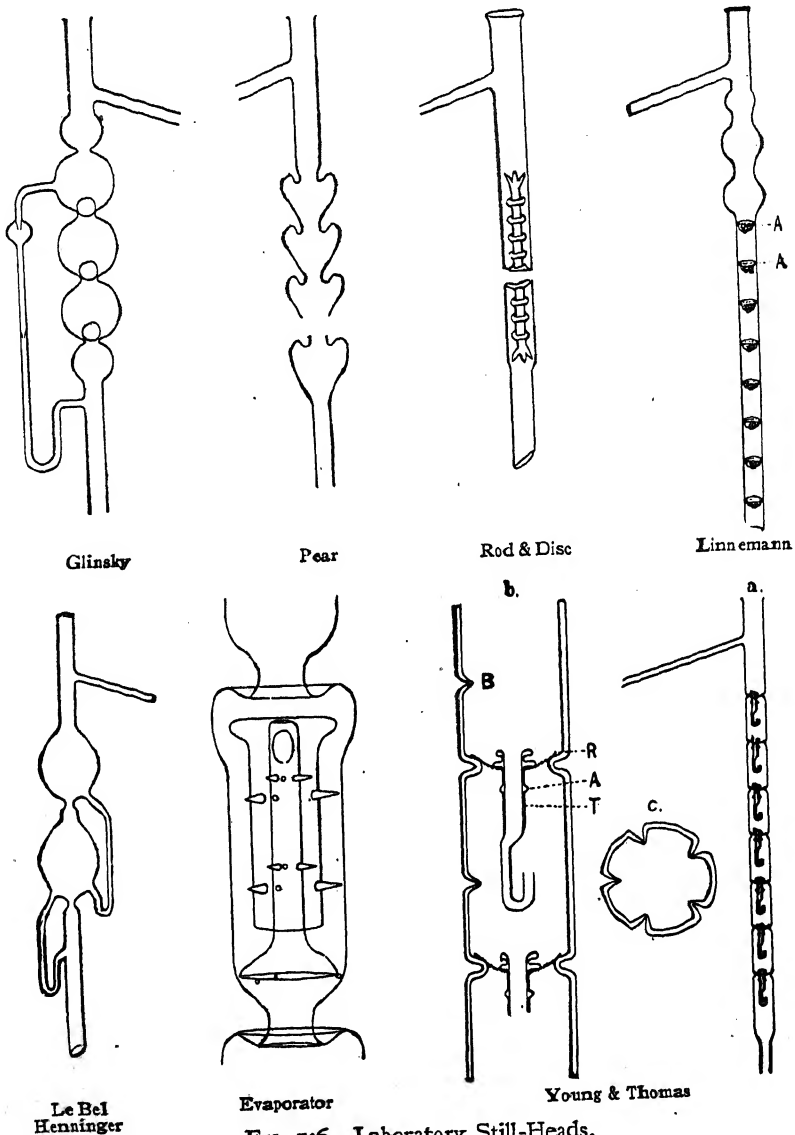


FIG. 136.—Laboratory Still-Heads.

heretofore given, as this is what Young referred to as "efficiency."

Young's experimental results cannot be presented fully here. He showed that the effectiveness of a plain-tube head increased with the length. For tubes of approximately equal length, the effectiveness was least when the diameter was about 14 mm., and better for both greater

and lesser diameters. But a 5 mm. diameter was more effective than a 26 mm. tube. The "rod and disc" still-head is more effective than the plain-tube. The downward flow of the liquid on the central rod is slower, greater surface of liquid is exposed to the vapor, and the liquid on the disc-rod is not cooled externally.

Young's Pear, a modification of the Wurtz-bulb, is more effective than the Wurtz-bulb, the "rod and disc," the plain-tube, the Glinsky, and the Le Bel-Henninger. The "Evaporator" and the "Young and Thomas" heads are clearly the most effective, as judged by Young's data, though the Hempel column is not far behind, and is better than the Pear.

The work of Young may be criticised on the ground that he compared the several still-heads without regard to their optimum capacity for distillation. Probably it would be fairer to make the comparison on the basis of a distillation rate that would be best for the particular head, without losing sight entirely of the practical value of time.

Golodetz[5] has designed a laboratory distillation-head of the types shown in Figure 137. These he compared with several other heads and found them to be superior to all of the others.

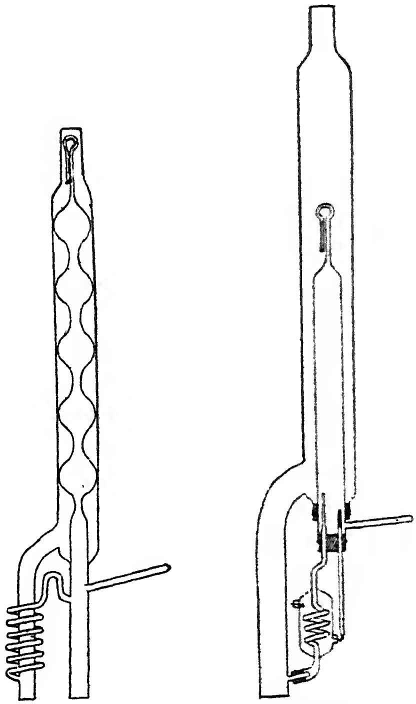


FIG. 137.—Golodetz Still-Heads.

Rittman and Dean[6] investigated various still-heads with reference to their use in distilling mixtures of petroleum hydrocarbons. Their results are shown in Table LXXIX and Figure 138. They concluded that the Glinsky, Le Bel-Henninger, "Young and Thomas," Golodetz, "Hempel column," "Rod and Disc," and the "Evaporator" were so nearly of the same effectiveness that the choice among them could be made on the basis of practical factors. They considered that the Le Bel-Henninger, Pear, and "Rod and Disc" were eliminated because they flooded and failed to pass the vapors as moderate temperatures were reached. The Golodetz gave erratic results in their hands. The Young and Thomas and the "Evaporator" are too fragile and complicated. The Glinsky is less effective, and also fragile. So the con-

[5] *Chem. Ind.*, 35 (1912), 102-8, 141-5.

[6] *J. Ind. Eng. Chem.*, 7 (1915), 185-195, 754-760. Also U. S. Bur. Min., *Bull.* 125.

TABLE LXXIX

RITTMAN AND DEAN'S DATA ON EFFECTIVENESS OF STILL-HEADS

SUMMARY OF RESULTS OF DISTILLING PENNSYLVANIA CRUDE OIL IN VARIOUS TYPES OF APPARATUS, SHOWING AVERAGE PERCENTAGE DISTILLED AT TEMPERATURES OF 100° TO 325° C.

Series No.	Type of Apparatus	Average Percentage Distilled										
		100° C.	125° C.	150° C.	175° C.	200° C.	225° C.	250° C.	275° C.	300° C.	325° C.	Up to 150° C.
1	Allen-Jacobs	0.0	1.0	5.0	7.6	7.8	7.5	7.0	6.7	6.2	6.6	6.0
2	Retort (B).......	0.5	2.5	8.7	8.3	8.3	8.3	6.8	6.5	7.4	...	11.7
3	Lunge	1.0	4.0	7.4	8.4	7.6	7.0	6.5	6.3	7.4	...	12.4
4	Engler-Ubbelohde.	2.8	5.4	7.7	7.4	7.1	7.0	6.9	6.8	...	...	15.9
5	Plain distilling tube	3.1	4.8	7.4	8.1	7.5	6.9	7.0	7.2	...	...	15.3
6	Two-bulb Wurtz .	4.4	5.3	7.0	...	...	...	...	...	...	...	16.7
7	Four-bulb pear ...	4.4	5.5	8.5	7.1	6.5	6.1	6.7	7.0	...	...	18.4
8	Norton-Otto	4.9	5.7	6.7	6.8	7.2	...	...	...	...	...	17.3
9	De Konink	4.8	5.6	6.9	6.7	7.0	6.6	6.6	7.0	...	...	17.3
10	Twelve-bulb pear .	5.7	6.7	6.1	7.1	7.0	6.1	...	...	...	...	18.5
11	Glinsky	5.6	5.8	7.6	7.1	6.2	6.8	6.6	6.8	...	...	19.0
12	LeBel-Henninger..	5.9	5.8	7.0	6.1	6.7	...	...	...	...	...	18.7
13	Young-Thomas ...	5.7	5.8	6.2	6.7	6.7	6.4	6.2	6.9	...	...	17.7
14	Golodetz	6.2	5.7	6.4	8.0	7.9	8.5	8.0	...	...	...	18.3
15	Six-inch Hempel .	6.3	6.3	6.0	6.8	6.3	6.4	6.5	7.0	...	...	18.6
16	Rod and disc.....	6.5	5.9	6.4	7.0	6.3	6.5	7.1	...	...	...	18.8
17	Evaporator	6.6	6.0	6.7	7.1	6.3	6.1	6.7	6.9	...	...	19.3

clusion was reached that the Hempel column was the simplest and best of the several still-heads. A column 6 inches long and of 1 inch diameter filled with 5 inches of aluminium beads was favored. The flask used by Rittman and Dean is shown in Figure 139. Aluminum beads were found to give only slightly better results than glass beads as a filling material.

H. F. Taylor[7] has designed a laboratory head called the "Plate and Bulb" that simulates the construction of the sectional column used in plant practice. This is shown in Figure 140. The column consists of a glass tube 14 in. long, and 1 1/16 in. in diameter, containing nine lead discs, 1 1/16 in. in diameter, supported by the copper wire spacers. The glass bulbs are so blown as to fit the holes in the lead plates. The bottom of the bulb is flared as shown so that the flare cannot be pulled through the hole in the plate.

The vapor from the distilling flask condenses in part, and collects on the lead plates. The liquid does not run through the holes in the plates, since the vapor is passing up through these, but when it accumulates sufficiently to float the glass bulb an opportunity is given for return flow. Taylor claims that this apparatus has the practical advantage over many others that it will effectively distill liquids with as low a

[7] *J. Soc. Chem. Ind.*, 37 (1918), 238-9R.

boiling point as 46° C. or as high as 200° C., whereas, as is well known, other apparatus, as, for example, the LeBel-Henninger, floods as the boiling point of the liquid increases.

Taylor compared several forms of laboratory still-heads by distilling three mixtures:

1. Carbon Disulfide and Benzene. 100 cc. of a mixture of equal volumes was distilled at a rate of 3½ cc. per minute. The per cent of CS_2 was determined in the first 45 cc. distilled.

2. Denatured alcohol (94.7 per cent) and Water. 200 cc. of a mixture of equal volumes of these liquids was distilled at a rate of

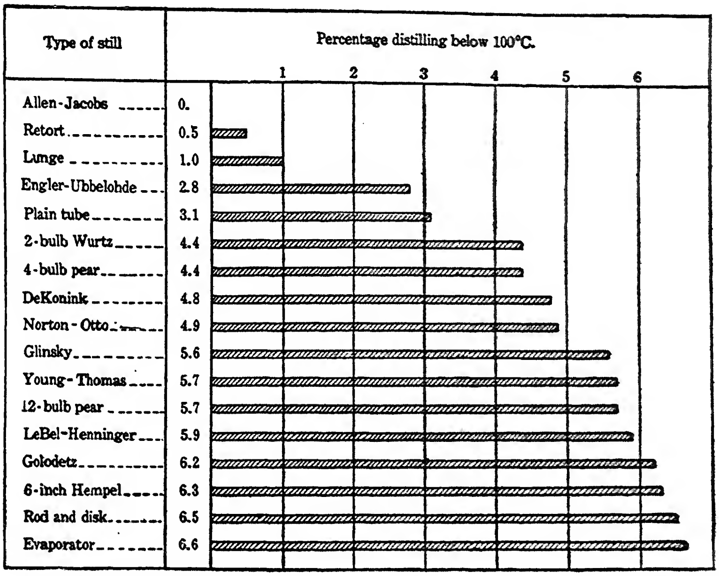


FIG. 138.—Graphical Showing of Rittman and Dean's Comparison of Still-heads.

3½ cc. per minute. The per cent of alcohol in the first 95 cc. collected was determined in each case.

3. Toluene and Pyridin. 100 cc. of a mixture of equal volumes was distilled at a rate of 3 cc. per minute. The percentage of toluene in the first 45 cc. of distillate was determined.

The results are shown in Table LXXX.

A still-head that is particularly useful for distilling very small quantities of liquid has been designed by S. F. Dufton.[8] This type is shown in Figure 141. The working-space of the column consists of an annular spiral, made by winding copper wire around a glass tube held concentrically within the outer glass tube. These heads can be large or small. A successful one used by Dufton was 150 cm. long, outer

[8] *J. Soc. Chem. Ind.*, 38 (1919), 45-6T.

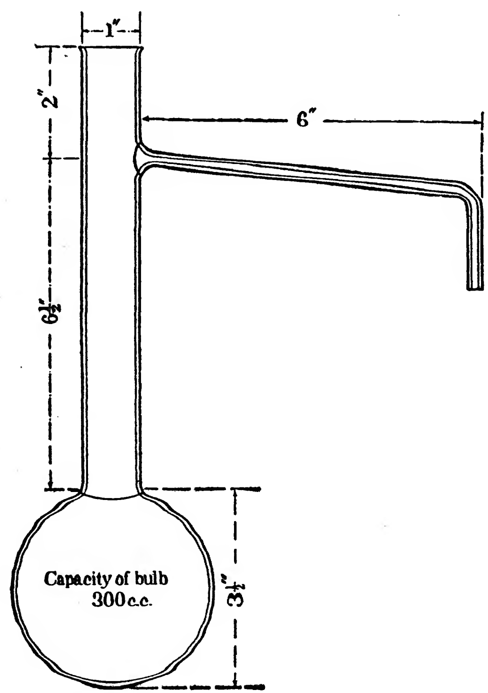


Fig. 139.—Rittman and Dean Distilling Flask.

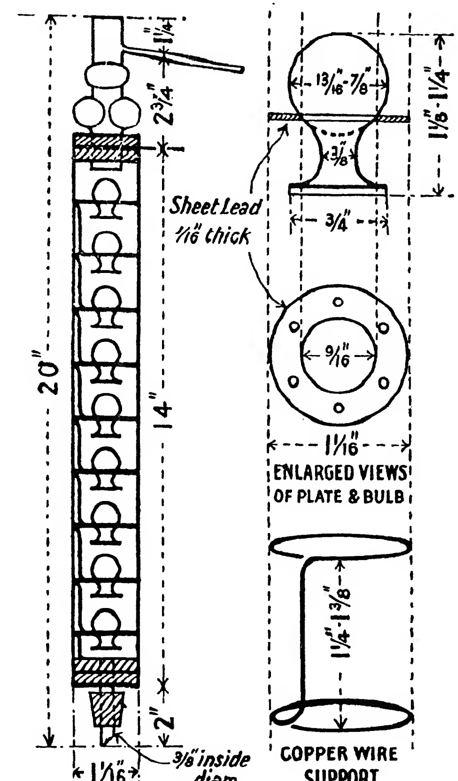


Fig. 140.—Taylor's "Plate and Bulb" Head.

TABLE LXXX

Taylor's Data on Effectiveness of Still-heads

Fractionating Column Used	Total Length in Inches	Mixture 1 Per Cent CS_2 in 1st 45 cc. Distilled	Mixture 2 Per Cent Alcohol in 1st 95 cc. Distilled	Mixture 3 Per Cent Toluene in 1st 45 cc. Distilled
Retort	....	69.9	....	....
Flask without column	....	70.0	....	62.6
Glinsky	15½	74.2	....	....
Young's "Rod and Disc"	20	78.6	....	....
Young's "Pear"—12 bulbs	23	79.4	88.4	70.0
Young's "Evaporator"—3 sections	20½	....	88.0	....
LeBel-Henninger—4 bulbs	20	80.1	88.1	71.5
Hempel Column — 7½" x 1 1/16" of ¼" — 3/16" beads	21	86.1	....	73.0
Hempel Column — 12" x 1 1/16" of ¼" — 3/16" beads	21	89.7	....	....
Two LeBel-Henninger heads. 8 bulbs altogether	36	91.1	....	....
Taylor's "Plate and Bulb" column	20	90.6	91.0	75.6

tube 17 mm. I.D., inner tube 13 mm. O.D., and closed at each end, wire 1 mm. diameter and wound with a pitch of 18 mm. at the top and 22 mm. at the bottom. The column was protected by a 2-in. layer of cotton wadding covered with asbestos yarn. During the operation of the column the liquid seals the small spaces between the wire and the glass tubes so that vapor and liquid contact thoroughly, but flow easily, in the spiral annulus. This column was found to be far more effective than Young's "Pear." From 100 cc. of a mixture of equal volumes of benzene and toluene it was found possible to distill 45 cc. of pure benzene at constant temperature. The initial distillation rate was 4 cc. per minute. During the collection of the 46th cc. the temperature rose 0.1° C. and the distillation rate decreased. On increasing the size of the flame, the temperature rose rapidly to the boiling point of toluene, and remained constant beginning with the 55th cc.

Another still-head of the same general type was built by Dufton, in the use of which 4.6 cc. of benzene, 9.4 cc. of toluene, 0.7 cc. of intermediate cut, and 0.3 cc. loss, were the products obtained upon distilling a mixture of 5 cc. of benzene and 10 cc. of toluene. This head was 120 cm. long, and consisted of four spiral sections varying from a 1.4 mm. tube wound with 0.7 mm. wire in the top section to a 1.4 mm. tube wound with 1.4 mm. wire in the bottom. The pitch of the spiral winding increased from 6 mm. at the top to 12 mm. at the bottom.

An investigation of the merits of various still-heads that presents some interesting features has been carried out by J. Friedrichs.[9] He

[9] *Z. f. Angew. Chem.*, 32 (1919), 340-4.

points out the difficulty of making fair comparisons, and mentions the importance of rate of distillation. His apparatus is shown in Figure 142. The delivery tube is of capillary size at C, so that the pressure rises if the distillation rate is too fast. The pressure cuts off a portion of the gas supply in regulator D. The jacket G was not used in all experiments, but served, with its auxiliaries H, F, K, and L, to control the temperature about the column. Friedrichs' results are too voluminous to be reproduced in detail, but Figure 143 shows part of them in graphic form.

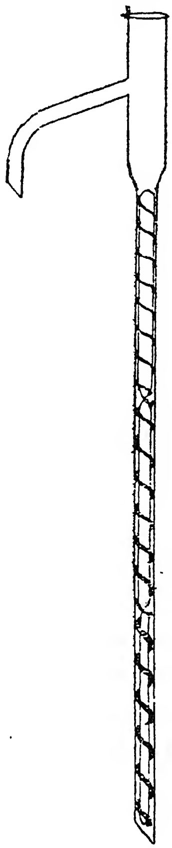


FIG. 141.—Dufton's Spiral Still-Head.

The regulator worked well, as an inspection of the distillation data shows a constant distillation-rate. In each experiment 150 cc. of a mixture of equal volumes of benzene and toluene was distilled. The key to the curves of Figure 143 is as follows:

1. Ordinary flask with side-tube.
2. Wurtz with two 4 cm. diam. bulbs.
3. Glinsky with three 3 cm. diam. bulbs, and balls for sealing each tube.
4. Hempel with 2.8 cm. of glass ball filling. Diameter of tube 1.5 cm.
5. Hempel with 35 cm. of glass ball filling. Diameter of tube 3 cm.
6. Tin coil in boiling benzene (dimension ?).
7. Plucker[10] head—This is a Hempel column modified so as to be heated externally by a warm stream of air. Contained 17 cm. of glass beads in an annular space 3 to 2 cm. in diameter.
8. Simplified Plucker with the Hempel column in boiling benzene. 29 cm. of glass beads. Diameter of tube 1.5 cm.
9. Hempel-Winssinger[11] with water temperature-control. 28 cm. column of glass beads. Diameter of tube 15 cm.
10. Same as 9, but temperature held constant at 70 to 71° C. where water entered, and 76 to 77° C. where it left.
11. Hempel with 58 cm. of glass filling. Diameter 3 cm. Tube surrounded by boiling toluene or its vapor.

The most interesting feature of Friedrichs' results lies in a comparison of the operation of the Hempel column at room temperature and at other temperatures controlled by the various heating media in the jackets. Still-head No. 8 gave a much better result than No. 4.

[10] *Chem. Ztg.*, 37 (1913), 1441.
[11] *Chem. Ztg.*, 10 (1886), 371.

Number 9 was better than No. 8 as far as the distillation was carried. Number 9 was nearly the same as No. 10, and No. 11 was the best of all. Casual interpretation of these results might lead to the conclusion that a regulated-temperature still-head was better than one without regulation. This would be contrary to the theoretical development of the subject of distillation. The joker lies in the fact that all laboratory still-heads, as ordinarily used, function in some degree as

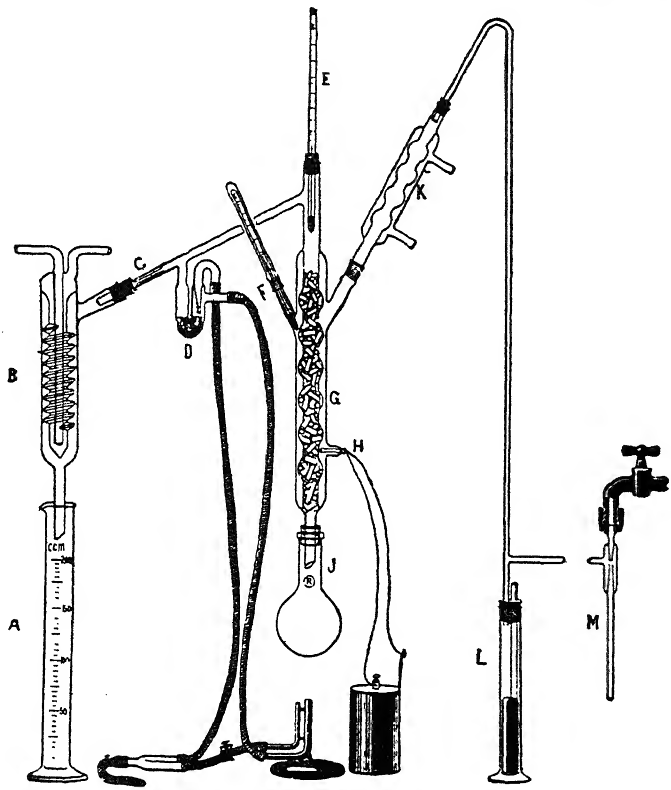


FIG. 142.—Friedrichs' Apparatus.

regulated-temperature heads. The lower the temperature of the medium surrounding the head the poorer the results of the distillation. This is shown in Friedrichs' experiments with still-heads Nos. 8, 9, 10 and 11. Had head No. 11 functioned in such a manner that the temperature inside the still-head was 110.6° C. at 760 mm. (the b.p. of toluene), no fractionation would have taken place. The entire vapor would have passed through the head unchanged in composition. As a matter of fact, condensed and cooled toluene was running back from the jacket-reflux. Heat was taken up to some extent by the distilling column,

but not in a degree sufficient to influence unfavorably the adjustment of phase-composition and temperature. Heads Nos. 8, 9, and 10 are simply milder editions of No. 11 as used in Friedrichs' experiments. The danger of using theory in design, without taking into account other theoretical considerations such as heat transfer in this instance, is clearly illustrated. Oversights of this nature often lead to condemnation of

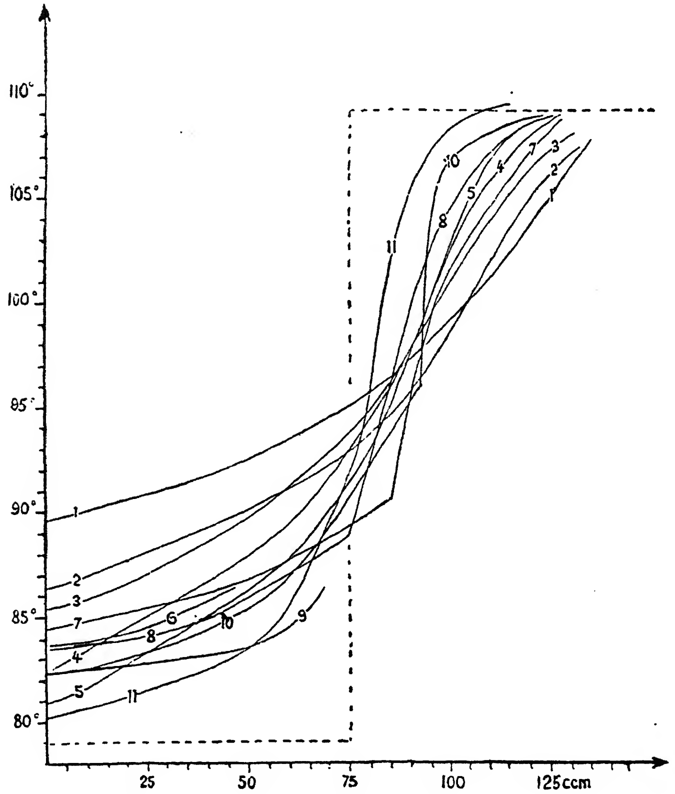


FIG. 143.—Graphical Showing of Friedrichs' Comparison of Still-Heads.

"theory," when actually the difficulty lies in the narrowness of view and knowledge of the designer. More often than not the necessary fundamental data are lacking, and it is then that intelligent experimentation may somewhat empirically point the way to correct design or operation.

A further point of interest in Friedrichs' experiments lies in the fact that he used a constant distillation rate. This was done to make the results comparable, but is done at the sacrifice of effective separation. The curves would present a far more favorable appearance if he had

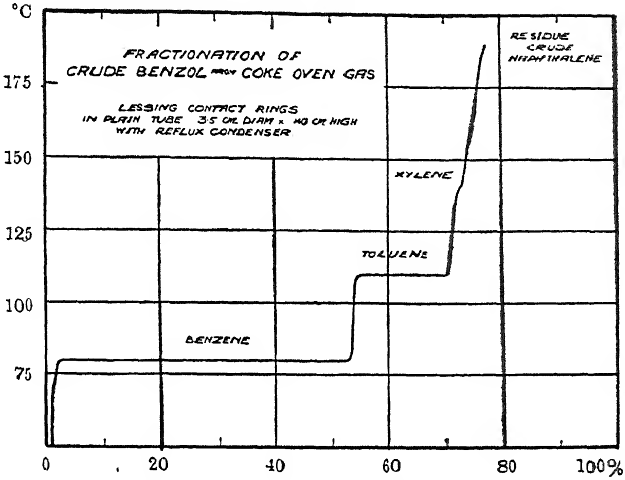


FIG. 144.—Distillation Curve of Crude Benzol. Lessing Head Used.

used a constant flame, and then allowed the distillation rate to be greatest at first and almost nil just before the change of receiver for collection of the middle fraction.

R. Lessing[12] reports the results of distillations made by using a laboratory still-head packed with ¼ in. x ¼ in. aluminum rings of the

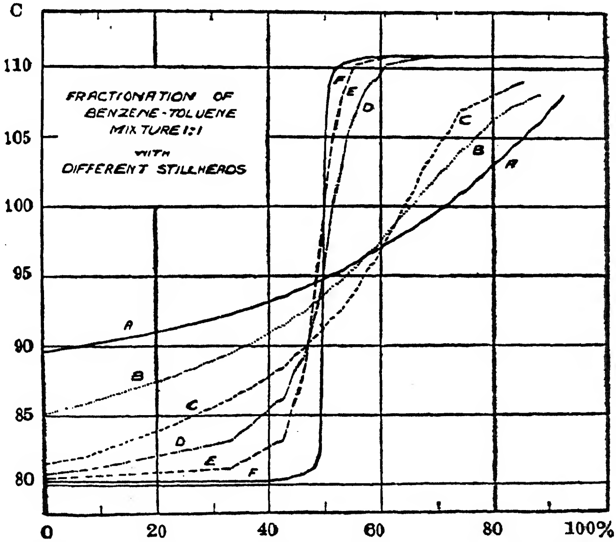


FIG. 145.—Distillation Curves of a 50:50 Benzene-Toluene Mixture. Various Still-Heads Used.

[12] *J. Soc. Chem. Ind.*, 40 (1921), 115T-119T.

Raschig type as modified by Lessing. The still-head was 4 cm. wide, and 140 cm. high. The distillation rate was 1 drop per second. Figure 144 gives the distillation curve obtained in distilling a crude benzol. Sharp fractionation is clearly indicated. Figure 145 shows the distillation curves obtained on fractionating a 1 : 1 mixture of benzene and toluene. The plain tube filled with Lessing rings is shown to be an effective still-head.

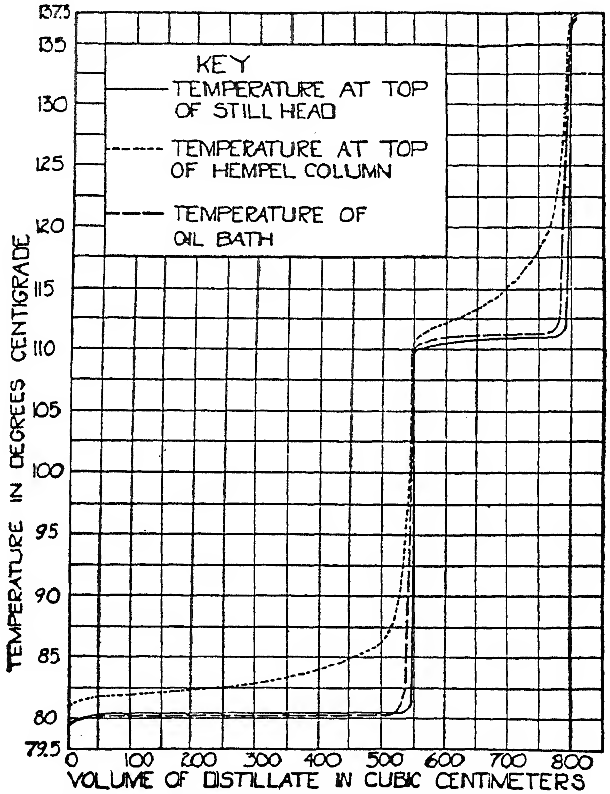


FIG. 146.—Distillation Curves of Coal-Tar Light Oil.

Lessing advocates the use of cooling in a reflux, rather than depending on condensation within the column. This begins to sound like business. He also suggests the use of electrical heating of the column to minimize heat loss therefrom by conduction and radiation.

F. M. Washburn [13] describes the design and use of an Hempel-column combined with a constant-temperature still-head. His column

[13] U. S. Bur. St., Tech. Paper 140, Oct. 18, 1919. *J. Ind. Eng. Chem.*, 12 (1920), 73-77.

was not effective as Lessing's as can be seen from Figure 146. Washburn showed that he could accurately analyze various mixtures of aromatic hydrocarbons.

N. P. Moore[14] has discussed the subject of fractional distillation in a qualitative way, and has made distillation studies with a specially constructed metallic still-head. As is so frequently done, he has confused effectiveness with efficiency, but the article in general will be found of interest, and numerous references to the literature are given.

Leslie-Geniesse Distillation Apparatus.[14a]

An apparatus that is based on fundamental principles, and that has been found both effective and efficient in practice, is shown in Figure 147. The features of this apparatus may be enumerated as follows:

1. Countercurrent flow and intimate contact of liquid and vapor phases are utilized. The apparatus is therefore based on the most efficient process for producing changes in compositions of vapor and liquid. Intimacy of contact of vapor and liquid is assured by filling the inner tube of the column with $\frac{3}{16}$-in. or $\frac{1}{4}$-in. thin sheet-metal cylinders of the Raschig, Lessing, or other type. Other effective packings made from thin sheet-metal can also be used. These types of packing offer large surface without sacrifice of free-space. They are far superior to glass beads, aluminum beads, metal balls, or any other packing of this type.

2. The tube containing the column-packing is surrounded by a glass jacket. The annular space between these tubes is highly evacuated in order that the transfer of heat from the inner tube outwards shall be as poor as possible. The apparatus is also well lagged, although this is not shown in the figure. The tubes should be made of glass rather than metal because glass is a poorer conductor of heat than metal. The ideal condition would be to have no heat loss whatsoever from the inner tube containing the packing. Two bulges or bulbs are blown on the jacket tube in order to take up the strains that result on account of the difference in temperature, and hence in expansion, of the inner and outer glass tubes.

3. The heat is supplied by passing an electric current through a submerged resistance coil. This coil should be placed in a bulb blown on the bottom of the flask containing the liquid. This allows vaporization of all, except a few cc., of the liquid in the flask. The resistance coil must offer enough surface so that the heat produced as a result of the passage of the electric current is transferred to the liquid without overheating the coil and thus causing decomposition of the liquid. Electric heating is preferable to gas heating because of the ease of

[14] *J. Phys. Chem.*, 25 (1921), 273-303.

[14a] An apparatus of this general type was suggested by me to Mr. John Dion who made preliminary studies of its effectiveness and efficiency in the Chemical Engineering Laboratories at the University of Michigan. Mr. John C. Geniesse has continued these studies, and is using the apparatus in connection with experimental studies of distillation phenomena.

control and the accuracy with which energy input can be measured if desired.

4. The reflux,[15] or weight of liquid returned to the column, can be controlled in a number of ways. The type of reflux, or partial-condenser, shown in Figure 147 may be operated by passing a regulated volume of gas or liquid, whose temperature is thermostatically controlled, through the jacket of the reflux. The temperature of the fluid in the reflux jacket may be held constant if desired, or may be automatically varied in a continuous and progressive manner suitable to the particular case. The temperature change of the fluid in the reflux jacket may be measured as indicated by use of a differential thermometer if so desired.

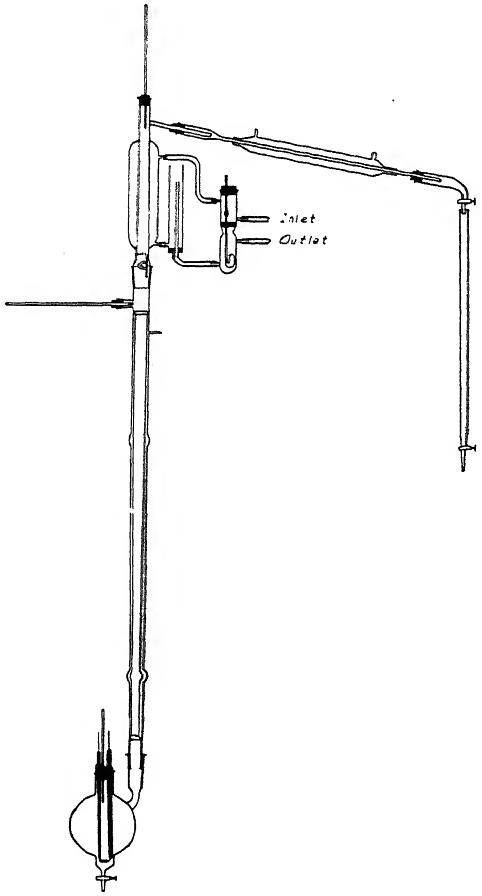


FIG. 147.—Leslie-Geniesse Distillation Apparatus.

Another type of reflux is shown diagrammatically in Figure 148. The liquid in the jacket may be a single substance or a mixture. The heat-loss from the reflux depends largely on the surface of the inner tube in contact with the boiling liquid in the jacket, and on the temperature difference between the vapor from the column and the boiling point of the liquid in the jacket. The rate of heat removal from the reflux can be controlled by varying the nature and composition of the liquid in the jacket, by varying the depth of liquid in the jacket, or both. This type of reflux is of particular value ... distillation.

...ations covering novel features of reflux design and operation ...hese processes and apparatus are applicable in plant as well ...ctice.

In Figure 148 the liquid is indicated at (1), a connection to a regulated overflow, if desired, or to drain liquid from the reflux is shown at (2), and a connection to a trap and filling tube at (3).

It will be recalled that the weight of liquid returned to the column from the reflux is a function of the composition of the liquid in the still. Various automatic means can be used to vary the heat-loss in the reflux, and thus vary the weight of liquid returned to the column as a function of the composition of the liquid in the still. By choice of proper means and method of refluxing the apparatus shown in Figure 147 can be adapted to the quantitative separation of binary mixtures, or to the separation, to a remarkable but not quantitative degree, of complex mixtures such as petroleum or petroleum distillates. A single distillation of petroleum will of course effect a quantitative measurement of the "gasoline," or other distillate of arbitrarily chosen distillation range, from petroleum. The limit to which plant practice should approach is easily and definitely established.

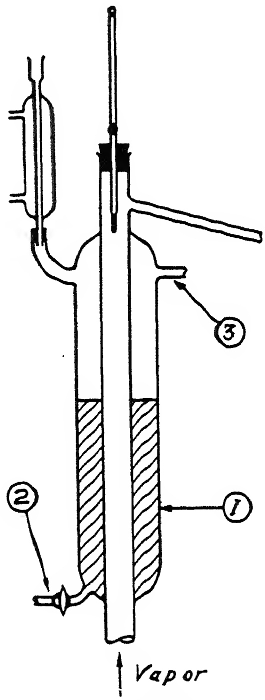


FIG. 148. — Leslie-Baker "Latent-Heat" Reflux.

A more detailed description of this distillation apparatus and its application will be published shortly. As an example of the effectiveness of the separation possible, the distillation curve of a mixture of equal parts by weight of chloroform and toluene is shown in Figure 149. The size of the intermediate cut collected as the temperature rises from the boiling point of chloroform to that of toluene is a function of the weight of liquid distilled as well as of the effectiveness of the apparatus. As the last small weight of chloroform is separated from the toluene in the flask, the vapor is pushed up the column by vapor containing more and more toluene until finally pure toluene is being vaporized in the flask. Not only is the separation most difficult at this stage, but the length of the column operating on mixed vapor becomes less and less. If it is desired to reduce the intermediate fraction as far as is reasonably possible, a relatively large weight of liquid must be distilled through a column of small volume, and the rate of distillation must be very slow when the intermediate cut is approached and separated. A long column of small diameter and filled with a ⅛-in. packing that drains liquid freely is desirable. However, it is unnecessary to go beyond reasonable limits in these regards for quantitative separations can be made without using freakish apparatus. In all cases the weight of liquid refluxed should

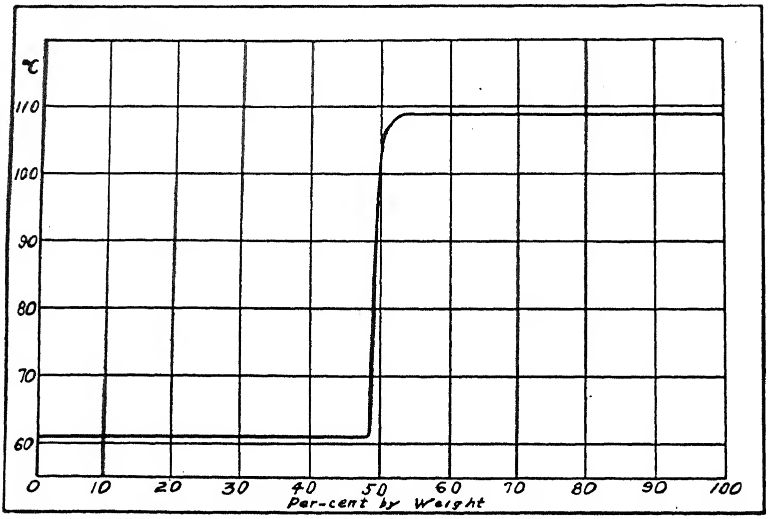
be based on a "L_R" or "reflux" curve determined by a series of points calculated by methods apparent from the context of Chapter IV.

Distillation Technique.

The following notes on several phases of laboratory distillation technique are by no means complete treatments of the subjects, but may be found helpful.

Source of Heat for Distillations.

The gas burner is an unsatisfactory source of heat in many ways because of variability in the flow of gas, effects of draughts, and diffi-



49.—Distillation Curves Illustrating the Effectiveness of Leslie-Geniesse Apparatus.

...rate adjustment. Adequately sized supply pipes, and pro- ...erning the gas pressure will partly remedy the first of ... A burner such as the Tirrell may be adjusted far more ...new needle-valve spindle is provided with fine thread ...pering point. An accurately dimensioned hole of ...usual should be drilled into a threaded plug that may ...ping the regular needle-valve seat.

...special gas burners have been devised. Probably the most satisfactory of these is the one used by the Atlantic Refining Company.[16] This is shown in Figure 150.

[16] *J. Ind. Eng. Chem.*, 10 (1918), 823.

External electrical heaters have been used to a limited extent in the distillation of oils. Their advantages are thought to be ease of regulation, and constant heat supply. These are in fact the advantages of electrical heaters so constructed that the heat capacity of the heater is small. If the heat capacity is large, ease of regulation, and flexibility are lost. In general, the submerged resistance coil will be found more satisfactory than an external electrical heater.

An electrical heater is described by Dean [17] and is said to have proved satisfactory in use in the laboratories of the U. S. Bureau of Mines. Commercial modifications of this heater can be purchased from dealers in laboratory supplies.

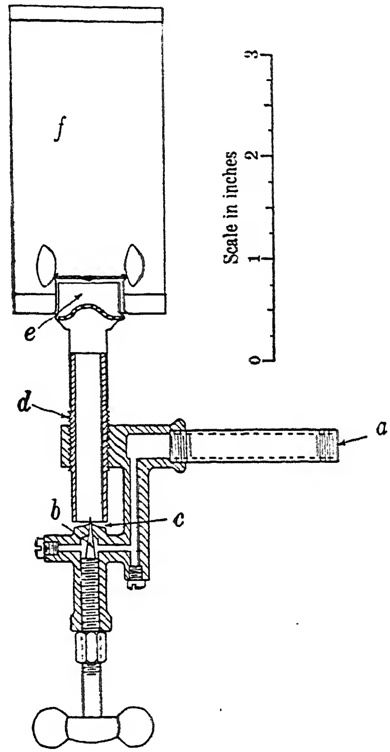


FIG. 150.—Atlantic Refining Co. Gas Burner.

T. W. Richards and J. H. Mathews [18] described an electrical heater that is immersed in the liquid to be distilled. They observed that the liquid boiled at a much more constant temperature when heated by the passage of an electric current through the immersed coil than when heated in the ordinary way with a gas flame. This difference they ascribed to the difference in the extent of superheating in the two cases. The apparatus used is shown in Figure 151. The value of the method of heating was shown by two experiments alike in all respects except in the manner of heating. Six ordinary distillations were required to obtain 75 cc. of butyl alcohol (b.p. 117.0 to 118° C. at 759 mm.) from 100 cc. of a specimen of the dry alcohol. Only two distillations were required to obtain 75 cc. of a better product (b.p. 117.3 to 117.9° C.) when the immersed heater was used.

The coil shown in Figure 151 consisted of 40 cm. of platinum wire with a resistance of 0.7 ohm. A current of 10 to 15 amperes was led to the coil by copper leads (2.5 to 3.0 mm. diameter, so that vapor will not be superheated) encased in glass tubes into the ends of which the platinum wire was sealed. Contact between the platinum and copper

[17] *J. Ind. Eng. Chem.*, 10 (1918), 823-26.
[18] *J. Am. Chem. Soc.*, 30 (1908), 1282-84.

wires was made by means of a drop of mercury. The coil must be completely immersed at all times. The ebullition takes place without bumping. High boiling liquids are distilled as successfully as very volatil liquids.

A distillation apparatus, useful for the exact measurement of boiling points of liquids and for the preparation of moderate quantities of pure liquids, has been described by Richards and Barry.[19] Precise thermometric measurements can be made in this apparatus. Their technique should prove of value in laboratory work involving preparation and study of the properties of many hydrocarbon substances.

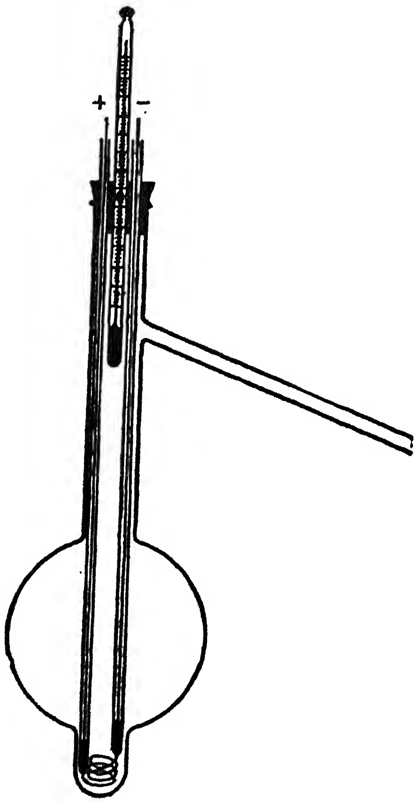


FIG. 151.—Richards-Mathews Submerged Heating-Coil.

The Regulation of Pressure During Distillation.

The regulation of pressure during a distillation is necessary in precise work. John Wade and R. W. Merriman [20] describe an apparatus and procedure suitable for pressure regulation during distillation. The detailed description of this and other apparatus for this purpose is too lengthy to be included here. The appended list of references covers the field in part:

HOLTERMANN, J. W., *Chem. Ztg.*, 22 (1908), 8.

RIEFF, H. J., *Z. f. Angew. Chem.*, 22 (1909), 1360.

WILLSTÄTTER, MAYER, HÜNE, *Ann.*, 378 (1910), 149.

VILLIERS, A., *Chem. Abs.*, 5 (1912), 806-7, 3639.

BECKMANN, E., *Zeit. Physik. Chem.*, 79 (1912), 565-76.

ANON., *Lum. Elec.*, 25 (1915), 124.

BECKMANN AND LIESCHE, *Zeit. Physik. Chem.*, 88 (1914), 13-21.

GHEORGHIU, V., *Chem. Abs.*, 10 (1916), 1709.

ANON., *Chem. Ztg.*, 43 (1919), 811.

SMITH, L., *J. Prakt. Chem.*, 102 (1921), 295-304.

Miscellaneous.

Fractional distillation is so widely used in the laboratory that a volume could be written on special technique and apparatus. Much useful information is contained in Young's "Fractional Distillation,"

[19] *J. Am. Chem. Soc.*, 36 (1914), 1787-91.
[20] *J. Chem. Soc.*, 99 (1911), 984-97.

and in books on laboratory methods. More will be found in the original literature. A recent article by P. Gross and A. H. Waight[21] presents a description of several interesting apparatus. The following quotations are taken from their article.

"PROTECTION OF CORKS.

"It is very often necessary to fractionate liquids, the vapors of which either attack or exert a solvent action on cork or rubber stoppers. The usual methods of wrapping the stopper with tin or silver foil are only occasionally successful, and sometimes (as with high-boiling corrosive liquids like chloroacetic acid) fail utterly, necessitating recourse to expensive all-glass stills.

"The device shown in Fig. 152 overcomes this difficulty. It consists of a small ball condenser which condenses the hot vapor and keeps it from reaching the stopper. If the bulb is blown from Pyrex tubing or other good grade of glass no fear need be entertained of its cracking on account of the temperature extremes to which it is subjected.

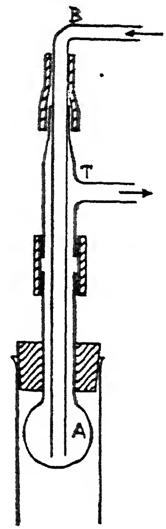


FIG. 152. — Device for Protecting Stoppers.

"MICRO-DISTILLING FLASK.

"Occasion often arises to distill and determine the boiling point of as little as from 0.5 to 2 cc. of liquid. If the liquid is pure the value can readily be determined by the submerged bulblet method.[22] In most cases, however, the liquid is a mixture, and it is necessary to separate the constituents and to learn the boiling points of the fractions to aid in their identification. The apparatus shown in Fig. 153 consists of a small bulb, A, about 1 cm. in diameter, with a side tube, B, sealed to it, which is the inner tube of the Condenser C. In the top of A is a narrow well, about 0.5 cm. deep, made by softening the top of the bulb and pushing in with a charred wood sliver. In this well is put a drop of mercury about 1 mm. deep, into which dips the tip of a copper-constantin thermo-couple.[23] The couple is best calibrated in the still by means of liquids of known boiling points.

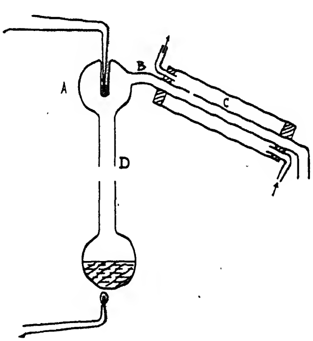


FIG. 153.—Micro-Distilling Flask.

[21] *J. Ind. Eng. Chem.*, 13 (1921), 701-3.
[22] Smith and Menzies, *J. Am. Chem. Soc.*, 32 (1910), 897.
[23] Constructed as recommended by White, *J. Am. Chem. Soc.*, 36 (1914), 1868, 2011, 2292, and Adams, *Ibid.*, 36 (1914), 72. Instead of using an elaborate

"RECEIVER FOR VACUUM FRACTIONATIONS.

"Many attempts have been made to solve the problem of changing receivers in a vacuum distillation without altering the pressure of the system. These are of two types: the first employing a by-pass controlled by stopcocks.[24] In the second type (Bruhl, Bredt, Gautier) the receivers are rotated (by means of a lubricated joint or connection) beneath the common spout delivering the distillate. Those of the first type have the disadvantage that the new receiver must be exhausted to the same pressure as the system, and they involve all the troubles attendant on the use of a number of stopcocks blown in a closed glass ring which is easily fractured.

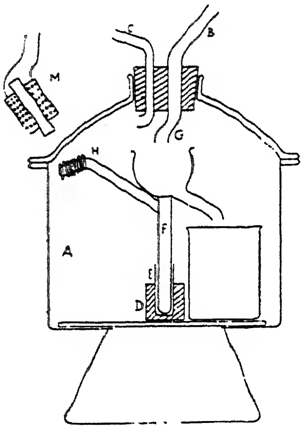


FIG. 154.—Receiver for Vacuum Fractionations.

"The second type is more convenient, but at low pressures it is exceedingly difficult to keep the complicated moving joint or connection airtight and in proper alignment. In the receiver shown in Fig. 154 these objections are eliminated. In the desiccator, A, the revolving funnel, F, receives the distillate from G and is turned to the appropriate receiver from without by the strong magnet, M, acting on the iron wire armature, H. Tube C governs the vacuum.

"VACUUM GAGE.

"Since for some substances the increase of vapor pressure with temperature is so slow, in a vacuum distillation a change of as much as a degree in boiling temperature may (especially at low pressures) result from a millimeter change in pressure. If the definition of the temperature is to be made to 0.1°, as is sometimes necessary in a fractional vacuum distillation, the pressure must be measured to 0.1 mm. The ordinary absolute manometer is not capable of this accuracy unless great pains are taken with its construction and filling, and special adjuncts (such as a vernier) are provided to aid the eye in estimating the tenths of a millimeter. The gage illustrated in Fig. 155 is a modified McLeod gage, but has several advantages (for the purpose

potentiometer, if great accuracy is not desired, there may be used a millivoltmeter, or better, one of the numerous compact, portable instruments now available which utilize the potentiometer principle.

[24] Since writing this our attention has been called by Professor A. B. Lamb to a similar piece of apparatus described by Palomaa, *Chem. Ztg.*, 1902, 337. This method seems, however, to be generally unknown, although the only one which will accomplish the desired purpose simply and efficiently.

in hand) over the usual forms of the latter. It is quick operating, direct reading, and simple in construction. The 10-cc. pipet A (closed at C) is calibrated so that volume v between C and H is one-eleventh of the volume V between C and K. At D a leveling tube F at least 90 cm. long is connected. The side tube B is 30 to 40 cm. long, and has a millimeter scale back of it whose 0 lies at H. The leveling tube F is filled with sufficient mercury to keep a seal when the mercury stands at the top of B. The system whose pressure is to be measured is attached to B. On raising F till the mercury stands at H in CH, the height HI in cm. is equal to the pressure in millimeters. By reading HI to 0.5 mm., the pressure is given to 0.05 mm.

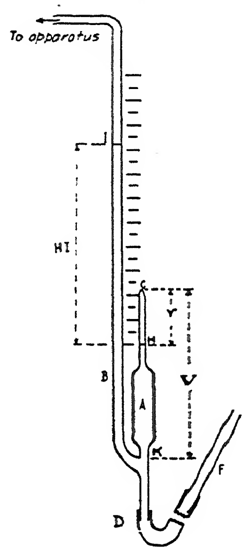


FIG. 155.—Vacuum Gage.

"The principle of the gage and its calibration is as follows: Let P be the pressure in the system to be measured. Before raising F this will also be the pressure in A. On raising F a volume of gas V is trapped in A, and its compression to volume v forces the mercury up in B to I. Let the pressure in v be p. This is greater than that in the system by the height HI cm. of mercury. Then by the gas laws:

$$pv = PV \quad \text{and}$$
$$p = PV/v$$
$$\text{Also} \quad HI = p - P$$
$$\text{Therefore} \quad HI = P(V/v - 1)$$
$$\text{By the calibration} \quad V/v = 11$$
$$\text{Therefore} \quad HI = P(11 - 1)$$
$$\text{and} \quad P = HI/10$$

Therefore the height HI, in centimeters, is equal to the pressure in millimeters. It is obvious that by changing the ratio V/v the sensitivity of the gage can be changed. Also in a given instrument two or more marks on CH with the accompanying knowledge of the volume ratios will increase the range of the gage. The one described will, however, be found the most convenient for general use, reading to 0.1 mm. or better up to 30.0 mm., thus covering the range for most vacuum distillation."

A frequent problem encountered in distillation procedures is joint leakage. Collodion is sometimes used with success for making tight joints, but a glue such as LePage's is more effective.

When a flask is used over and over for the distillation of hydrocarbon liquids a black deposit is formed on the bottom. This is difficult to remove by the means usually tried, but is easily loosened by application of a caustic soda solution of moderate strength.

References.

The references cited in this chapter will be found to contain an abundance of further references to the original literature, enough in fact to serve as the nucleus of a complete bibliography on the subject matter covered in the foregoing discussion.

Chapter XVI.

Methods of Analysis.

Specific Gravity.

The specific gravity of motor fuel and distillates may be determined by the use of the hydrometer, the specific gravity balance, or the picnometer. These are mentioned in the order of increasing accuracy.

The true specific gravity of a substance is the ratio of the weight (in vacuo) of unit volume of the substance at 60° F. to the weight (in vacuo) of unit volume of water at 60° F. The weighings are made with brass weights and corrected for the weight of the air displaced by the weights.

Specific gravities as measured by the several types of instruments are not true, but apparent, specific gravities. Apparent specific gravity is sometimes defined as the ratio of the weights in air (50 per cent humidity, at 60° F. and at 760 mm. pressure) of unit volume of the substance and of water, when the weighings are made with brass weights of 8.4 density. The corrections are so small that it is necessary to apply them only to picnometer measurements, since these only are of an order of accuracy such as to warrant the correction.

The Hydrometer.

This is the simplest of all the instruments used to determine specific gravities, and, if calibrated and used properly and carefully, measurements of very fair accuracy can be obtained.

An hydrometer consists of a weighted elongated glass bulb attached at one end to a slender graduated glass tube. When placed in a liquid it sinks until the weight of the volume of the liquid displaced is equal to the weight of the hydrometer. Obviously the instrument will displace a smaller volume of a heavy liquid than lighter liquid. The volume of liquid displaced by an hydrometer varies inversely as the specific gravity of the liquid. Since the hydrometer is graduated so that the figures on the stem indicate equal increments in specific gravity it is evident that the graduations are not spaced the same distance apart. As the specific gravity increases the distance between graduations on the hydrometer stem decreases.

The Baumé hydrometer, which is so commonly used in oil work, is so made that the scale reads in arbitrary degrees. These are not ratios as are specific gravities. It is important to know the formula or "modulus" that expresses the relationship for the particular scale that one is using. Two formulas are in use for liquids lighter than water.

The U. S. Petroleum Association in 1864 adopted a set of instruments graduated in accordance with the relationship

$$Bé._{L}^{\circ} = \frac{141.5}{\text{Sp. Gr. } 60^{\circ} \text{ F.}/60^{\circ} \text{ F.}} - 131.5$$

This formula has been widely used by the petroleum fraternity.

Another formula has been extensively used in other industries as well as by the petroleum industry, and has been used by the U. S. Bureau of Standards since 1904.

$$Bé._{L}^{\circ} = \frac{140}{\text{Sp. Gr. } 60^{\circ} \text{ F.}/60^{\circ} \text{ F.}} - 130$$

This formula is the basis of the conversion tables given in the "United States Standard Tables for Petroleum Oils."

Much confusion has arisen as a result of the use of these two scales. On January 23, 1922, the American Petroleum Institute sent a questionnaire to the industry which, in substance, was as follows:
1. Do you approve of the modulus 141.5 as applied to the oil industry?
2. Do you approve that the scale be known as the "American Petroleum Institute Scale"?

The replies to this inquiry were almost unanimously affirmative. The Institute, the U. S. Bureau of Mines, and the U. S. Bureau of Standards have considered the matter and agreed that in the interest of uniformity of practice the modulus 141.5 be used exclusively by the petroleum industry, and be known as the "American Petroleum Institute Scale." Data are to be expressed as "Degrees A. P. I." to avoid confusion with the 140 modulus Baumé scale. The U. S. Bureau of Standards requests that the designation "Degrees Baumé," when referring to liquids lighter than water, be used only when the modulus 140 is the basis of calculations.[1]

For liquids heavier than water, Baumé degrees and specific gravity are related by the equation

$$Bé._{H}^{\circ} = 145 - \frac{145}{\text{Sp. Gr. } 60^{\circ} \text{ F.}/60^{\circ} \text{ F.}}$$

How to Read an Hydrometer.

The liquid should be placed in a clear glass cylinder and the hydrometer carefully immersed in it, to a point slightly above that to which it will sink, and then allowed to float freely. Wetting the stem slightly above the point of immersion avoids abnormal effects of surface tension. The hydrometer should be free from air-bubbles.

As soon as the instrument floats freely at rest the reading can be taken. The eye should be placed slightly below the plane of the surface of the oil and slowly raised until this surface, seen at first as an ellipse, becomes a straight line. The point at which this line cut the scale of the instrument should be taken as the reading.

In case the oil is too dark in color to allow of this method of read-

[1] Chem. Met. Eng., 26 (1922), 1120.

ing it is necessary to read from above the surface of the oil. Correction must then be made for the distance that the oil has crept up the stem of the hydrometer. This distance may be estimated by making readings from above and below on a clear oil of characteristics similar to the dark oil. A specific gravity hydrometer reads too low, and a Baumé hydrometer too high, when read at the upper edge of the meniscus. The correction must be applied accordingly.

A valuable and interesting paper on the Baumé hydrometer has been written by George H. Taber.[2] In addition to discussing the fundamental principles on which hydrometers are based, he points out some of the frequently misunderstood features of the Baumé hydrometer.

The divisions representing Baumé degrees are spaced equal distances apart on the stem of the hydrometer. This is the result of the fact that Baumé degree numbers are the reciprocals of a harmonic series of specific gravities, modified only by being multiplied by a constant and added to another constant. They form an arithmetic progression. The hydrometer is divided to indicate equal increments of immersion so that the corresponding specific gravity numbers form the harmonic series just referred to.

The Baumé scale is neither inaccurate nor unscientific. In fact, because of its equispaced divisions, it is more likely to be correctly graduated than the specific gravity hydrometer. The correctness of its divisions can be readily checked. Also it is easy to make accurate interpolations when readings are being made.

The disadvantage of Baumé readings is that, for some purposes, they must be converted to specific gravities before they can be used. If two liquids that show no volume change on mixing are to be blended to make a mixture of some chosen weight per unit volume it is necessary to know the specific gravities. An error, not uncommonly made, is to blend on the basis of degrees Baumé. This cannot be done, as a few simple calculations will show. For example a mixture of equal volumes of liquids of 10° Bé. and 70° Bé., if Baumé degrees are used as the basis of blending, should give a mixture of 40° Bé. However, the "gravity" is found to be 34.7° Bé., which is equivalent to 0.850 sp. gr., or the mean of the specific gravities 1.000 and 0.700 of the liquids.

On the other hand if *weights* are used in place of *volumes* blending calculations can be made in terms of degrees Baumé. Thus specific gravities and weights per unit volume are closely related; and Baumé degrees, light or heavy, are related, although more remotely, to volumes per unit weight. For further details reference should be made to Mr. Taber's paper.

The Specific Gravity Balance.

The specific gravity balance of the Westphal type is a most convenient instrument for taking specific gravities. A good instrument properly used to determine the gravity of non-viscous distillates should

[2] *J. Ind. Eng. Chem.*, 12 (1920), 593.

give readings that are not more in error than ± 2 in the fourth decimal place.

A balance of the ordinary type is shown in Figure 156. A beam, with pointer on one end and hook on the other, swings on a knife edge. A plummet, the weight of which is such as to exactly balance the beam in air, is suspended from the hook. The beam arm, between the fulcrum and the hook suspension, is divided into ten equal divisions. The weights are four in number. The mass of the largest is such that when

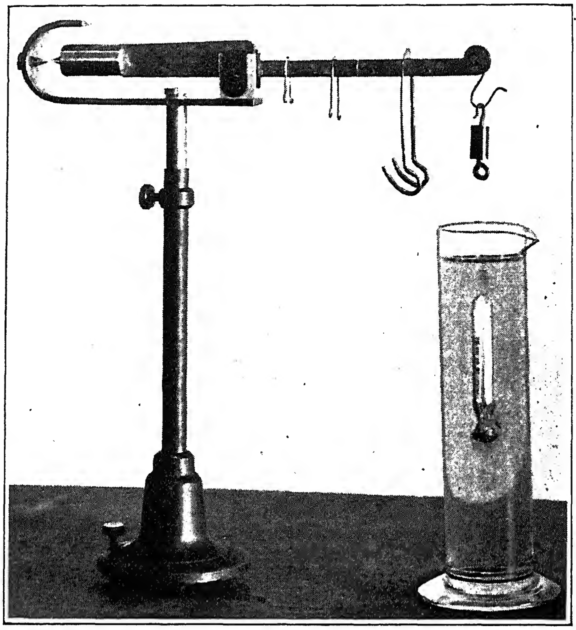


FIG. 156.—Specific Gravity Balance, Westphal Type.

hung on the hook its weight will bring the beam to equilibrium when the plummet is immersed in pure water at 60° F. The mass of the largest weight is thus equal to that of the water displaced by the plummet at 60° F. The second weight is $\frac{1}{10}$, the third $\frac{1}{100}$, and the smallest $\frac{1}{1000}$ the mass of the largest weight.

The balance should be set up, shielded from drafts, and adjusted, by means of the levelling screw, so that the end of the pointer comes to rest at, or swings evenly past, the fixed point, when the plummet is immersed in pure water at 60° F. The plummet should then be carefully dried and immersed in the liquid whose specific gravity is to be determined. The weights are placed on the beam, and the equilibrium of the beam restored. The position of the weights is then noted. That of the largest indicates the numeral to be written in the first

decimal place, and the others, in order of mass, the numerals to be written in the second, third, and fourth decimal places. The temperature of the liquid should also be recorded so that the specific gravity at 60° F. can be calculated.

Picnometer Method.

The picnometer method of determining specific gravities consists in determining the weight of a known volume of liquid. Many forms of picnometers and specific gravity bottles can be purchased from any dealer in laboratory supplies. For ordinary work the Sprengel picnometer shown in Figure 157 is probably the most satisfactory. The bulb-caps should be ground into the ends of the capillary tubes.

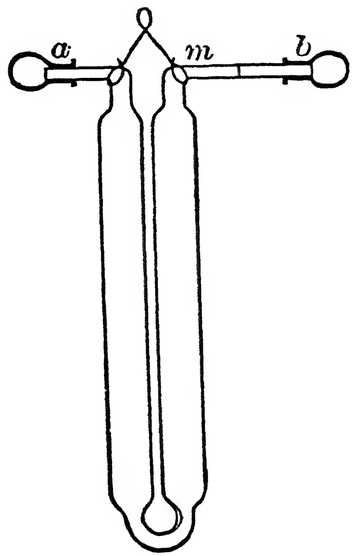


FIG. 157.—Sprengel Picnometer.

The picnometer must first be calibrated. To do this it must be thoroughly cleaned by the use of some suitable oxidizing cleaning mixture such as sodium dichromate and sulfuric acid, followed by washing with water, alcohol, and ether. Clean, dry air should be sucked through to remove the ether vapor. The weight of the picnometer is then taken on a good analytical balance. The instrument is then filled with distilled water that has been boiled for five minutes in a platinum or silver dish and cooled quickly to 55 to 60° F. The filled picnometer, without the caps, is then placed in a thermostat held at 60° F. While still in the thermostat a piece of filter paper is applied to the end of one of the capillary tubes. By this means water is absorbed until the meniscus in the other capillary exactly coincides with the mark. The clean dry caps are now placed on the ends of the capillary tubes, the picnometer is removed from the thermostat, dried, and carefully weighed. Should the liquid expand somewhat, because the room temperature is above 60° F., the caps will prevent loss of liquid. They also prevent evaporation. This is important when the picnometer is to be used for determining the gravity of volatil liquids.

The volume of the picnometer can now be calculated, for the weight of the water is known, and the weight of water per cubic centimeter at 60° F. can be found in any of the handbooks.

The picnometer is now dried in the same manner as before, and filled with the liquid whose gravity is to be determined. The procedure is the same as just given. The specific gravity is the ratio of

the weight of the liquid to that of the water, both of which filled the picnometer at 60° F.

For greater detail with regard to finesse in picnometer methods reference should be made to the standard works, on physical and chemical measurements, listed at the end of this chapter. Technologic Paper No. 77 of the U. S. Bureau of Standards, "Density and Thermal Expansion of American Petroleum Oils," also contains much valuable information on picnometric methods.

Correction of Specific Gravities for Temperature.

The U. S. Bureau of Standards[3] has shown that the change of specific gravity with change of temperature is the same for all distillates and oils of the same specific gravity. It had been believed that the coefficient of expansion of California oils was much higher than that of the Mid-Continent and Eastern oils, but the difference was found to be very small. The Bureau of Standards has therefore published the "United States Standard Tables for Petroleum Oils" as Circular No. 57. The tables in this document should be used to correct specific gravities at one temperature to the standard temperature of 60° F.

If the reading is expressed in "Degrees A. P. I." it should be converted to specific gravity, and then corrected for temperature. If an absolutely accurate correction is not required it may be made by reference to Table II. in Circular No. 57. For example, a distillate of 60 gravity A. P. I. at 80° F. is found in Table II. to have a gravity of 57.8° A. P. I. at 60° F. 60 gravity A. P. I. corresponds to 0.7389 sp. gr. This at 80° F. is equivalent to 0.7469 sp. gr. at 60° F., which expressed in degrees A. P. I. is 57.9. An error of 0.1° A. P. I. is thus involved in using the Baumé, i.e., 140-modulus, temperature correction table in connection with readings in A. P. I. or 141.5-modulus degrees.

Conversion Tables.

On account of the voluminousness of the tables of Circular No. 57 they are not included in full in this book. Abbreviated tables showing corresponding specific gravities and degrees A. P. I., and also showing corresponding specific gravities and degrees Baumé are given in Chapter XVII.

The coefficient of expansion of distillates and oils can be determined by the use of some form of dilatometer, but is more accurately measured by determining the density of the liquid at several temperatures. Reference should be made to Technologic Paper No. 77 of the U. S. Bureau of Standards for a discussion of this method.

Index of Refraction.

...bbé refractometer is best adapted to the determination of the ...fraction of distillates and oils. This instrument and the ...ing it are described in several of the standard analytical ...at the conclusion of this chapter.

[3] ...ndards, Tech. Paper 77.

Care must be taken in working with gasoline, or similar mixtures containing volatil components, that none of the most volatil portion vaporizes. The sample should be brought to 60° F. and a small portion of it flowed between the prisms from a small pipette. The refractive indices as thus determined should not differ by more than 2 in the fourth decimal place. The instrument should be operated at or near 60° F. A correction of 0.00021 should be added to the index for each 1° F. that the temperature of measurement was above 60° F., or subtracted for each 1° F. below 60° F. The standard temperature for the measurement of index of refraction is 60° F., and correction to this temperature should always be made.

Distillation Range.

Methods of distillation in the laboratory are discussed in Chapter XV, and it is the intention here to present only standard routine procedures.

The following is the method for the distillation of gasoline as given by the Interdepartmental Petroleum Specifications Committee.[4]

The Interdepartmental Petroleum Specifications Committee has published "Methods of Testing Petroleum Products" as Technical Paper No. 298 of the U. S. Bureau of Mines, dated April, 1922. The methods in this manual supersede those of Bulletins 1 to 5 of the Committee on Standardization of Petroleum Specifications.

Distillation of Gasoline.

(Method 100.1 Interdept. Pet. Spec. Comm.)
(A. S. T. M. Method D86-21T.

APPARATUS

1. *Flask*.—The standard 100-cc. Engler flask is shown in Figure 158, the dimensions and allowable tolerance being as follows:

DIMENSIONS OF ENGLER FLASH

Description	Centimeters	Inches	Tolerances (cm.)
Diameter of bulb, outside	6.5	2.56	0.2
Diameter of neck, inside	1.6	.63	.1
Length of neck	15.0	5.91	.4
Length of vapor tube	10.0	3.94	.3
Diameter of vapor tube, outside.	.6	.24	.05
Diameter of vapor tube, inside..	.4	.16	.05
Thickness of vapor tube wall...	.1	.04	.05

[4] The Interdepartmental Petroleum Specifications Committee was formed under authority of Circular 42 of the Bureau of the Budget, dated October 10, 1921, and Executive Order 3578, dated November 8, 1921. It replaced the Interdepartmental Committee on Standardization of Petroleum Specifications, which in turn superceded the war-time Committee on Standardization of Petroleum Specifications. The work of the several committees has been continuous.

The position of the vapor tube shall be 9 cm. (3.55 inches) ± 3 mm. above the surface of the liquid when the flask contains its charge of 100 cc. The tube is approximately in the middle of the neck and set at an angle of 75° (tolerance ± 3°) with the vertical.

2. *Condenser.*—The condenser (Fig. 159) consists of a 9/16 inch OD No. 20 Stubbs gage seamless brass tube 22 inches long. It is set at an angle of 75° from the perpendicular and is surrounded with a cooling bath 15 inches long, approximately 4 inches wide by 6 inches high. The lower end of the condenser tube is cut off at an acute angle, and curved downward for a length of 3 inches and slightly backward so as to insure contact with the wall of the graduate at a point 1 to 1¼ inches below the top of the graduate when it is in position to receive the distillate.

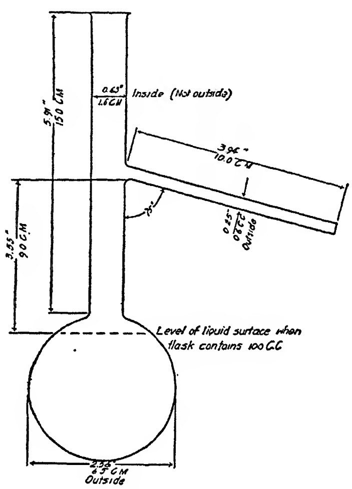


Fig. 158.—Standard 100 c.c. Engler Flask for Use in Making Distillation Tests of Gasoline and Kerosene.

3. *Shield.*—The shield (Fig. 159) is made of approximately 22-gage sheet metal and is 19 inches high, 11 inches long, and 8 inches wide, with a door on one narrow side, with two openings, 1 inch in diameter, equally spaced, in each of the two narrow sides, and with a slot cut in one side for the vapor tube. The centers of these four openings are 8½ inches below the top of the shield. There are also three ½-inch holes in each of the four sides, with their centers 1 inch above the base of the shield.

4. *Ring support and hard asbestos boards.*—The ring support is of the ordinary laboratory type, 4 inches or larger in diameter, and is supported on a stand inside the shield. There are two hard asbestos boards, one 6 by 6 by ¼ inch, with a hole 1¼ inches in diameter in its center, the sides of which shall be perpendicular to the surface; the other, an asbestos board to fit tightly inside the shield, with an opening 4 inches in diameter concentric with the ring support. These are arranged as follows: The second asbestos board is placed on the ring and the first or smaller asbestos board on top so that it may be moved in accordance with the directions for placing the distilling flask. Direct heat is applied to the flask only through the 1¼-inch opening in the first asbestos board.

5. *Gas burner or electric heater.*—(*a*) *Gas burner.*—The burner is so constructed that sufficient heat can be obtained to distill the product at the uniform rate specified below. The flame should never be so large that it spreads over a circle of diameter greater than 3½ inches

on the under surface of the asbestos board. A sensitive regulating valve is a necessary adjunct, as it gives complete control of heating.

(*b*) *Electric heater.*—The electric heater, which may be used in place of the gas flame, shall be capable of bringing over the first drop within the time specified below when started cold, and of continuing the distillation at the uniform rate. The electric heater shall be fitted with an asbestos board, top ⅛ to ¼ inch thick, having a hole 1¼ inches

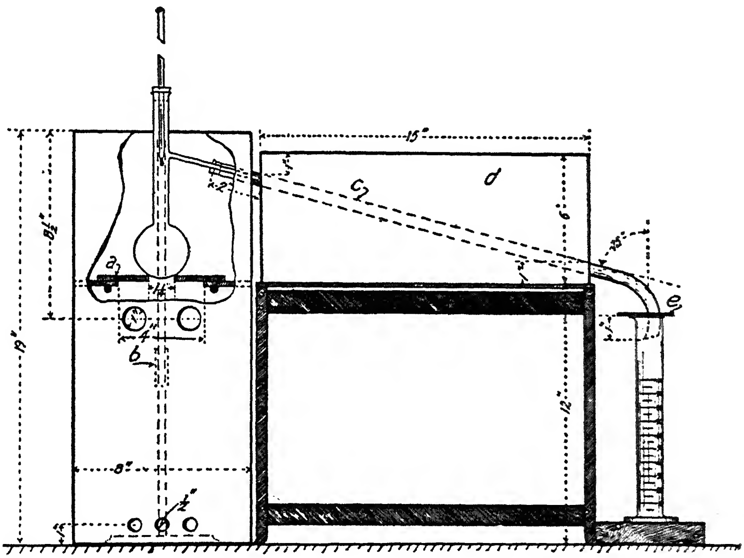


Fig. 159.—Standard Distillation Outfit.

in diameter in the center. When an electric heater is employed the portion of the shield above the asbestos board shall be the same as with the gas burner, but the part below may be omitted.

6. *Thermometer.*—A. S. T. M. low-distillation thermometer shall conform to the following specifications:

Type: Etched stem glass.
Total length: 381 mm.
Stem: Plain front, enamel back, suitable thermometer tubing; diameter 6 to 7 mm.
Bulb: Corning normal, Jena 16 III, or equally suitable thermometric glass; length, 10 to 15 mm.; diameter, 5 to 6 mm.
Actuating liquid: Mercury.
Range: 30° F. to 580° F., or 0° C. to 300° C.
Immersion: Total.

Distance to 30° F. or 0° C. mark, from bottom of bulb: 100 to 110 mm.

Distance to 580° F. or 300° C. mark, from top of stem: 30 to 45 mm.

Filled: Nitrogen gas.

Top finish: Glass ring.

Graduation: All lines, figures, and letters clear cut and distinct; scale graduated in 2° F., or 1° C. divisions and numbered every 20° F., or 10° C., the first and each succeeding 10° F. (5° C.) line to be longer than the others.

Special markings: "A. S. T. M. low distillation," Serial Number, and manufacturer's trade-mark etched on the stem.

Accuracy: Error at any point on scale shall not exceed one-half smallest scale division.

Test for permanency of range: After being subjected to a temperature of 560° F., or 290° C., for 24 hours the accuracy shall be within the limit specified.

Points to be tested for certification: 32°, 212°, 400°, 570° F., or 0°, 100°, 200°, 300° C.

NOTE. Until January 1, 1924, the thermometer specified on page 6 of Bulletin 5 of the Committee on Standardization of Petroleum Specifications may be used in place of the above thermometer.

7. *Graduate.*—The graduate shall be of the cylindrical type, of uniform diameter, with a pressed or molded base and a lipped top. The cylinder shall be graduated to contain 100 cc. and the graduated portion shall be not less than 7 inches nor more than 8 inches long; it shall be graduated in single cubic centimeters, and each fifth mark shall be distinguished by a longer line. It shall be numbered from the bottom up at intervals of 10 cc. The distance from the 100-cc. mark to the rim shall be not less than 1¼ inches nor more than 1¾ inches. The graduations shall not be in error by more than 1 cc. at any point on the scale.

PROCEDURE.

8. (*a*) The condenser bath shall be filled with cracked ice[5] and enough water added to cover the condenser tube. The temperature shall be maintained between 32° and 40° F. (0° and 4.45° C.).

(*b*) The condenser tube shall be swabbed to remove any liquid remaining from the previous test. A piece of soft cloth attached to a cord or copper wire may be used for this purpose.

(*c*) The bulb of the distillation thermometer shall be covered uniformly with a long-fiber absorbent cotton weighing not less than 3 nor more than 5 mg. A fresh portion of clean cotton shall be used for each distillation.

(*d*) One hundred cubic centimeters of the product shall be measured in the 100-cc. graduated cylinder at 55° to 65° F. (12.78° to

[5] Any other convenient cooling medium may be used.

18.33° C.) and transferred directly to the Engler flask. None of the liquid shall be permitted to flow into the vapor tube.

(*e*) The thermometer provided with a cork shall be fitted tightly into the flask so that it will be in the middle of the neck and so that the lower end of the capillary tube is on a level with the inside of the bottom of the vapor outlet tube at its junction with the neck of the flask.

(*f*) The charged flask shall be placed in the 1¼-inch opening in the 6 by 6 inch asbestos board with the vapor outlet tube inserted into the condenser tube. A tight connection may be made by means of a cork through which the vapor tube passes. The position of the flask shall be so adjusted that the vapor tube extends into the condenser tube not less than 1 inch nor more than 2 inches.

(*g*) The graduated cylinder used in measuring the charge shall be placed, without drying, at the outlet of the condenser tube in such a position that the condenser tube shall extend into the graduate at least 1 inch but not below the 100-cc. mark. Unless the temperature is between 55° and 65° F. (12.78° and 18.33° C.) the receiving graduate shall be immersed up to the 100-cc. mark in a transparent bath maintained between these temperatures. The top of the graduate shall be covered closely during the distillation with a piece of blotting paper or its equivalent cut so as to fit the condenser tube tightly.

9. When everything is in readiness, heat shall be applied at a uniform rate, so regulated that the first drop of condensate falls from the condenser in not less than 5 nor more than 10 minutes. When the first drop falls from the end of the condenser the reading of the distillation thermometer shall be recorded as the *initial boiling point*. The receiving cylinder shall then be moved so that the end of the condenser tube shall touch the side of the cylinder. The heat shall then be so regulated that the distillation will proceed at a uniform rate of not less than 4 nor more than 5 cc. per minute. The reading of the distillation thermometer shall be recorded when the level of the distillate reaches each 10-cc. mark on the graduate.

After the 90 per cent point has been recorded, the heat may be increased because of the presence of the heavy ends which have high boiling points. However, no further increase of heat should be applied after this adjustment. The 4 to 5 cc. rate can rarely be maintained from the 90 per cent point to the end of the distillation, but in no case should the period between the 90 per cent and the end point be more than five minutes.

The heating shall be continued until the mercury reaches a maximum and starts to fall consistently. The highest temperature observed on the distillation thermometer shall be recorded as the *maximum temperature* or end point. Usually this point will be reached after the bottom of the flask has become dry.

The total volume of the distillate collected in the receiving graduate shall be recorded as the *recovery*.

The cooled residue shall be poured from the flask into a small

cylinder graduated in 0.1 cc., measured when cool, and the volume recorded as *residue.*

The difference between 100 cc. and the sum of the recovery and the residue shall be calculated and recorded as *distillation loss.*

ACCURACY.

10. With proper care and attention to detail, duplicate results obtained for initial boiling point and maximum temperature, respectively, should not differ from each other by more than 6° F. (3.33° C.).

A. S. T. M. Committee D-2 at the meeting June 26 to 30, 1922, recommended that Section 8 (c) of the above be omitted. This also applies to the distillation of kerosene given below.

Distillation of Kerosene.

(Method 100.2 Interdept. Pet. Spec. Comm.)

APPARATUS AND PROCEDURE.

The apparatus and procedure are the same as given in method for gasoline, with the following exceptions:

Paragraph 4: The hard asbestos board 6 by 6 by 1/4 inches shall have a hole 1 1/2 inches in diameter in its center.

Paragraph 6: The A. S. T. M. high-distillation thermometer shall conform to the following specifications:

Type: Etched stem glass.

Total length: 381 mm.

Stem: Plain front, enamel back, suitable thermometer tubing; diameter, 6 to 7 mm.

Bulb: Corning normal, Jena 16 III, or equally suitable thermometric glass; length, 10 to 15 mm.; diameter, 5 to 6 mm.

Actuating liquid: Mercury.

Range: 30° F. to 760° F., or 0° C. to 400° C.

Immersion: Total.

Distance to 30° F., or 0° C. mark from bottom of bulb: 25 to 35 mm.

Distance to 760° F., or 400° C. mark from top of tube: 30 to 45 mm.

Filled: Nitrogen gas.

Top finish: Glass ring.

Graduation: All lines, figures, and letters clear cut and distinct; scale, graduated in 2° F. or 1° C. divisions and numbered every 20° F. or 10° C., the first and each succeeding 10° F. (5° C.) to be longer than the others.

Special markings: A. S. T. M. High Distillation, serial number, and manufacturer's name or trade-mark etched on the stem.

Accuracy: Error at any point on scale shall not exceed one smallest scale division up to 700° F. or 370° C.

Tests for permanency of range: After being subjected to a tempera-

ture of 700° F. or 370° C. for 24 hours the accuracy shall be within the limit specified.

Points to be tested for certification: 32°, 212°, 400°, 700° F. or 0°, 100°, 200°, 370° C.

Volatility.

The commonly accepted criterion of the volatility of gasoline is the distillation curve obtained by plotting the data obtained by the standard distillation method. An interesting paper on volatility was recently presented before the American Petroleum Institute by R. E. Wilson.[6]

Color.

The color of light distillates is frequently judged by inspection of a 4-ounce sample bottle filled with the liquid. Though inexact, this examination is sufficient for many purposes. Comparison should be made to a sample bottle filled with pure water.

The Saybolt chromometer is in general use for determination of the color of naphthas and other light distillates. The Lovibond Tintometer is also occasionally used.

The Saybolt chromometer is shown in Figure 160. The Interdepartmental Petroleum Specifications Committee describes the instrument and gives a general method (No. 10.1) for its use as follows:

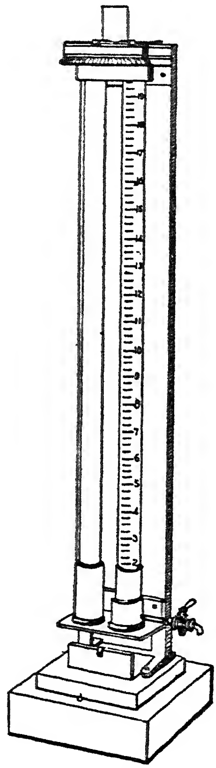


Fig. 160. — Saybolt Universal Chromometer.

APPARATUS.

The Saybolt chromometer consists of two similar glass tubes 20 inches long and about 5/8 inch in internal diameter. One tube is open at both ends, the other (the oil tube) is permanently closed at the bottom with a colorless glass disk, and is provided with a petcock on one side at the bottom. The tubes are supported in a vertical position above a mirror arranged to reflect light upward through the tubes. Above the tubes is an eyepiece so designed that the field of vision is equally divided between the two tubes. A standard yellow glass disk is placed at the bottom of the open tube.

PROCEDURE.

Place the apparatus at a north window so that only direct light from the sky is reflected upward through the tubes from the mirror. Clean

[6] *Bull. 203, Am. Pet. Inst.*, Dec. 30, 1921, 15-21.

the oil tube by running through it some of the sample to be tested. Fill the oil tube with the sample to be tested and compare the color of the 20-inch column of liquid with that of the standard yellow disk. If it is lighter than the standard, report it as + 25 Saybolt. If it is equal to the standard, report it as 25 Saybolt. If it is darker than the standard, draw off 2 inches of liquid and compare the color of the 18-inch column with the standard. If equal to standard, report as 24 Saybolt. If darker than standard, again draw off liquid in accordance with the following table:

SAYBOLT UNIVERSAL CHROMOMETER TABLE FOR DETERMINATION OF COLOR SHADES OF REFINED OIL

	Oil in Tube	Color Shade		Oil in Tube	Color Shade
	Inches	*Number*		*Inches*	*Number*
One disk	20	25	One disk	10⅝	20
Do	18	24	Do	9⅝	19
Do	16	23	Do	8⅝	18
Do	14	22	Do	7⅝	17
Do	12	[a] 21	Do	6⅝	[b] 16

[a] No. 21 color on the Saybolt chromometer is equal to the color of an aqueous solution of potassium bichromate containing 0.0048 gram per liter.
[b] No. 16 color on the Saybolt chromometer is equal to the color of an aqueous solution of potassium bichromate containing 0.0120 gram per liter..

As a check, draw off liquid in accordance with the table to lighten the color of the column one shade after it matches the standard.

By using two disks and a table furnished by the manufacturer the instrument may be used to measure the color of darker oils. Keep the instrument covered when not in use.

Subcommittee VI. of A. S. T. M. Committee D-2, which is engaged in a general study of the instruments used in the petroleum industry for the determination of color, in their report at the June, 1922, meeting of the Society, comment as follows on the Saybolt Chromometer:

"A thorough investigation of the Saybolt Chromometer shows many points which require consideration and action before the instrument can be put into satisfactory shape for use in a standard method. Some of the points under discussion are as follows:

"1. *Head.*—Several members of the sub-committee suggested that the head be improved by introducing refinement in the manufacture such as (1) a positive position for the prisms and (2) diaphragms to eliminate the shadows and make the reading more positive and accurate.

"2. *Position of Tubes.*—In the present instrument the position of tubes is not sufficiently fixed, and it is possible for tubes to be misaligned with openings in the head. Construction should be changed so as to make the position positive in all cases.

"3. *Diameter of Tubes.*—At the present time no limits exist for the internal diameter of tubes. Experimental work has shown definitely

that the internal diameter of the tube will affect the readings considerably.

"4. *Mirror.*—Question has been raised as to suitability of the mirror as a light reflector, due to the fact that the mirror reflects color as well as light. It has been suggested that this difficulty be overcome by use of suitable means to obtain diffused light.

"5. *Source of Light.*—The original directions with the Saybolt Chromometer call for use with northern daylight exposure. In view of the wide variations existing in daylight, the sub-committee is considering the use of an artificial daylight lamp."

The fundamental laws of color measurement are discussed, and a method that is claimed to be a rapid and accurate procedure for determining the true color of any and all petroleum distillates and oils is described by L. W. Parsons and R. E. Wilson.[7] They consider the method of the National Petroleum Association, and the Saybolt Chromometer as probably adequate for many commercial purposes, but of very little value for the accurate measurements required in research work. The Lovibond Tintometer is considered by them as superior to either of the foregoing instruments, but insufficiently accurate for scientific work. Parsons and Wilson use the Duboscq Colorimeter, and determine the depth of standard color solution necessary to match a layer of the oil of unknown color. The oil layer varies in thickness from a very thin film for the darkest oils to a 10 cm. layer when light oils are examined. The details of the method are too voluminous for reproduction here.

Reference should also be made to articles by C. E. K. Mees[8] and C. K. Francis,[9] and Paul D. Barton.[10]

Acidity.

The following test for acidity in gasoline is given by the Interdepartmental Petroleum Specifications Committee. It should be made immediately after the standard distillation test.

"Collect in a test-tube the cooled residue from the distillation flask, add 3 volumes of distilled water, and shake the tube thoroughly. Allow the mixture to separate and remove the aqueous layer to a clean test-tube by means of a pipette. Add 1 drop of a 1 per cent solution of methyl orange. No pink or red color shall be formed."

The method would obviously not detect weak organic acids, both because these acids are volatil and would distill, and because methyl orange is relatively insensitive to hydrogen ion. The color change of this indicator occurs when the H-ion concentration is about 10^{-4}. A method similar to that used for determining the acidity of heavier oils should be used when it is desired to determine organic, as well as strong acid, acidity.

[7] *J. Ind. Eng. Chem.*, 14 (1922), 269.
[8] *J. Ind. Eng. Chem.*, 13 (1921), 729-31.
[9] *Nat. Pet. News*, 13, June 10, 1921, 34-5.
[10] *Nat. Pet. News*, May 31, 1922, 53-4.

To 10 per cent of the distillate in an Erlenmeyer flask add 50 cc. of neutral 90 per cent ethyl alcohol. Shake thoroughly, and titrate with 1/10 Normal NaOH free from sodium carbonate. Two drops of 1 per cent phenolphthalein solution should be used as indicator. The result may be calculated in terms of H_2SO_4, or as the acid number, which is expressed as the number of milligrams of KOH required to neutralize the acids contained in 1 gram of the sample.

Corrosion.

The corrosion tests as given by the Interdepartmental Petroleum Specifications Committee are as follows:

Corrosion Test (Copper Dish). Method 530.1.

APPARATUS.

A freshly polished hemispherical dish of spun copper approximately 3½ inches in diameter.

MAKING A TEST.

Place 100 cc. of the gasoline to be examined in the dish and place the dish in an opening of an actively boiling steam bath, so that the steam comes in contact with the outer surface of the dish up to the level of the gasoline. Leave the dish on the steam-bath until all volatil material has disappeared.

INTERPRETATION OF RESULTS.

If the gasoline contains dissolved elementary sulphur or corrosive sulfur compounds, the bottom of the dish will be colored gray or black.

If the gasoline contains undesirable gum-forming constituents, there will be a weighable amount of gum deposited on the dish. Acid residues will show as gum in this test.

Corrosion Test at 122° F. Method 530.2.

(Copper Strip.)

Place a clean strip of mechanically polished pure sheet copper, about ½ in. wide and 3 in. long, and 10 cc. of the sample, in a clean test tube. Close the tube with a vented stopper, and hold in a thermostat for three hours at 122° F. Rinse the copper strip with sulfur-free acetone, and compare it with a similar strip of freshly polished copper. Discoloration or pitting indicate corrosion.

Corrosion Test at 210° F. Method 530.3.

(Copper Strip.)

This is the same as method 530.2 except that the tube is held at 212° F. instead of at 122° F.

Five-day Corrosion Test. Method 530.4.

Place clean strips of mechanically polished sheet brass, sheet steel, and sheet aluminum, about ½ in. wide and 3 in. long, in clean test tubes and add 10 cc. of the sample to be tested to each tube. Close the tubes with vented stoppers, and hold in a thermostat for five days at 210° F. At the end of this time rinse each strip with sulfur-free acetone, and compare it with a similar strip of the same metal freshly polished. Discoloration or pitting indicates corrosion.

Sub-committee XVII of Committee D-2 of the A. S. T. M. propose [10a] the following tentative method for the Detection of Free Sulfur and Corrosive Sulfur Compounds in Gasoline:

"A clean strip of mechanically polished pure sheet copper, about ½ inch in width and 3 inches in length, shall be placed in a suitable clean tube or sample bottle. Gasoline under test shall be added so that the copper strip is completely immersed. The test tube or sample bottle shall be closed with a loosely fitting cork, and held in a suitable bath at 122° F. (50° C.).

"At the end of three hours the gasoline exposed strip shall be removed and shall be compared with a similar strip of freshly polished copper.

"The presence of sulfur or corrosive sulfur compounds is indicated by the corrosion or discoloration of the gasoline exposed strip when compared with the fresh copper strip.

"Gasoline shall be reported as passing the test when on examination the exposed strip shows no discoloration as compared with the fresh copper strip.

"Gasoline shall be reported as not passing the test when on examination the exposed strip shows discoloration as compared with the fresh copper strip."

It is interesting to note in the report of this committee that of 36 variously designated samples of gasoline, examined by the foregoing "strip" test, all passed, whereas only 4 of these samples were given a clear "bill of health" by the "dish" test of the Interdept. Pet. Spec. Comm.

Gumming.

Sub-Committee XVII of Committee D-2 of the A. S. T. M. in their report at the June, 1922, meeting say, "No recommendation for a satisfactory gumming test can be offered at the present time, as results indicate that considerable work will be necessary to determine the controlling factors."

The determination of "gum" has been studied by N. A. C. Smith and M. B. Cooke.[10b] As I have already stated in Chapter XIV they found that gum formation depended on oxidation of olefins to alde-

[10a] Report of Committee at June, 1922, meeting.
[10b] Ser. 2394, U. S. Bur. Min., Sept., 1922.

hydes, which substances polymerize, or in some other manner, form gums. These facts must be taken into account in any method for determining "gum" in gasoline.

Evaporation of the gasoline out of contact with air is essential to the best accuracy, but is rather too time-consuming for routine work. The method adopted by Smith and Cooke consists in evaporating a 20-cc. sample of gasoline in a 30-cc. glass evaporating dish on a live steam-bath for four hours. The drying is completed by heating the dish and residue for 24 hours in an air-oven at 105° C.

Fused-silica and porcelain dishes were found unsatisfactory because the sample creeps when heated in dishes made of these materials. Larger glass dishes were also unsatisfactory because of the larger surface of gasoline exposed to oxidation.

Sulfur—Qualitative Methods,—the Doctor Test.

The doctor test is a qualitative test for H_2S, and for sulfur compounds that readily dissociate or split off H_2S. The test as given by the Interdepartmental Petroleum Specifications Committee is as follows:

PREPARATION OF REAGENTS.

"(1) Sodium plumbite (doctor solution).—Dissolve approximately 125 grams of sodium hydroxide in a liter of distilled water. Add 60 grams of litharge and shake vigorously for 15 minutes, or let stand with occasional shaking for at least a day. Allow to settle, and decant or siphon off the clear liquid. Filtration through a mat of asbestos may be employed if the solution does not settle clear. The solution should be kept in a tightly corked bottle and should be refiltered before use if not perfectly clear.

"(2) Sulphur. Pure dry flowers of sulphur.

MAKING OF TEST.

"Shake vigorously together in a test-tube 10 cc. of the sample to be tested and 5 cc. of sodium plumbite solution for about 15 seconds. Add a small pinch of flowers of sulfur, again shake for 15 seconds and allow to settle. The quantity of sulfur used should be such that practically all of it floats on the interface between the sample and the sodium plumbite solution.

INTERPRETATION OF RESULTS.

"If the sample is discolored, or if the yellow color of the sulfur film is noticeably masked, the test shall be reported as positive and the ... demned as 'sour.' If the sample remains unchanged in color, ... r film is bright yellow, or only slightly discolored with ... with black, the test shall be reported negative and the ... ed 'sweet.'"

The principles of the doctor treatment are discussed by S. Schwartz and H. G. Nevitt.[11]

The Sodium Sulfide Test.

Place a piece of metallic sodium about the size of a small pea in the bottom of a hand glass test-tube that is vertically supported. Heat the bottom of the tube, and, as soon as the sodium vapor forms a layer about ½ in. in height, drop in a single drop of the sample to be tested. At intervals add more of the sample, one drop at a time, until 5 or 6 drops have been added in all. Cool the tube, and remove any excess sodium by adding a little ethyl alcohol. Then cautiously add a little water, stir with a glass rod, rinse the contents of the tube into a small beaker, boil, and filter. The volume of the filtrate should be about 15 cc.

To test for sulfur add two or three drops of a dilute solution of sodium nitro-prusside to 1 cc. of the prepared solution. A violet color indicates that sulfur is present. The test is extremely delicate, and according to Dr. Mabery[12] can be used quantitatively if comparison of depth of color is made with colors developed by oils containing known per cents of sulfur.

The solution made as above can also be used to test qualitatively for nitrogen or the halogens.

Sulfur—Quantitative.

The quantitative methods for determining sulfur in petroleum oils include methods involving combustion in a lamp, combustion in oxygen under pressure in a Mahler-type bomb, heating with alkaline oxidizing mixtures, oxidation with nitric acid or nitric acid and bromine, and various modifications of these general procedures. The concensus of opinion seems to be that the Carius method is the most dependable when the oil contains more than a few hundredths of one per cent of sulfur, but that this method requires too much time. Lamp methods are regarded favorably and have been adopted as standard as indicated below. Combustion in the bomb is criticised because of the relatively small sample that can be taken, because the $SO_4^=$ may combine with the lead gasket, because combustion is not always complete, and because part of the sulfur is oxidized to SO_2 only, and not to SO_3. All methods such as the alkaline oxidizing treatments are open to the serious objection that it is impossible to precipitate pure $BaSO_4$ from a solution that contains salts of the alkali metals. These methods are also criticised because of loss of sulfur through volatilization or incomplete oxidation.

"Sulfur in Petroleum Oils" is the subject of Technologic Paper No. 177 of the U. S. Bureau of Standards, written by C. E. Waters. This paper should be consulted for a discussion of methods for determining

[11] *Pet.*, 7 (1919), No. 2, 23, 96, 98, 100 and 102. See also *Chem. Abs.*, 13 (1919), 2438-9.
[12] *J. Ind. Eng. Chem.*, 6 (1914), 102.

sulfur, and for many references to the literature of this subject. A few additional references are given below.[13]

Determination of Sulfur in Naphthas and Burning Oils.

The following method given as tentative by the American Society Test. Mat.[14] (Method D-90-21T) for the determination of sulfur in naphthas and burning oils. It is also given by the Interdepartmental Pet. Spec. Comm.[15] as a method for sulfur in burning oils. (Method 520.1.)

APPARATUS.

Absorber of chemically resistant glass, about 150 cc. capacity, containing glass beads or short pieces of glass rod in the suction side as shown.

Chimney of chemically resistant glass connected with the absorber by a rubber stopper.

Spray trap of chemically resistant glass connected with the absorber by a rubber stopper.

Small lamp of about 25 cc. capacity. This lamp may conveniently consist of a 25 to 35 cc. Erlenmeyer flask and a cork carrying a short section of glass tubing about 1/8 inch in inside diameter. The cork must be grooved along the sides so that air may enter the flask while the oil is being consumed.

Ordinary cotton wicking.

Filter pump or other means for continuous suction and rubber tubing to connect with spray trap.

SOLUTIONS REQUIRED.

Hydrochloric acid.—Solution containing 2.275 grams HCl per liter, carefully checked for accuracy.

Sodium carbonate.—Solution containing 3.306 grams Na_2CO_3 per liter. Exactly 10.0 cc. should be required to neutralize 10.0 cc. of the hydrochloric acid solution.

Methyl orange.—Solution in distilled water, containing 0.004 gram methyl orange per liter.

PROCEDURE.

Pass two strands of new cotton wicking about 4.5 inches long through the 1/8-inch diameter wick tube so that they are not twisted

[13] Christie and Bisson, *J. Ind. Eng. Chem.*, 12 (1920), 171-2. Waters, C. E., *J. Ind. Eng. Chem.*, 12 (1920), 482-5. Jackson and Richardson, *J. Inst. Pet. Tech.*, 7 (1921), 26-34. Bowman, S., *J. Inst. Pet. Tech.*, 7 (1921), 334-8. Esling, F., *J. Inst. Pet. Tech.*, 7 (1921), 83-96. Hauser, H., *Anales Soc. Espan. fis. Quin.*, 19 (1921), 175. Mabery, C. F., *Proc. Amer. Acad. Arts Sci.*, 30 (1894).

[14] *Proc. A. S. T. M.*, 21 (1921), 644-7.

[15] U. S. Bur. Min., Tech. Ppr. 298, 48-51.

but parallel in the wick tube. Trim the wick with very sharp scissors. Pour into the clean, dry lamp about 20 cc. of the oil to be tested, insert the wick, and cork and weigh the assembly with an accuracy of 0.001 gram. It is advisable to make a blank determination at the same time and under the same conditions by burning sulphur-free alcohol in a similar lamp.

Rinse the absorber containing the glass beads thoroughly with distilled water and add exactly 10.0 cc. of the standard sodium-carbonate solution from an accurately calibrated burette, allowing the burette to drain for three minutes before the reading is taken. Rinse the chimney and the spray trap with distilled water, dry the chimney, and connect both to the absorber as shown in Figure 161. Set up the apparatus for the blank determination in exactly the same manner, using exactly 10.0 cc. of the sodium-carbonate solution. Apply gentle suction to both absorbers, light both the weighed oil lamp and alcohol lamp, and then place in position under the chimneys, so that the tops of the wick tubes extend into the chimneys not more than 1/16 inch. Adjust the wick height and the suction so that the flame is steady, free from smoke, and approximately one-fourth inch high. This requires that the wick be flush with the top of the wick tube for naphthas and a little higher for illuminating oils. The room must be free from drafts. The suction on the blank should be so adjusted that air is drawn through both determinations at the same rate. Continue burning for about two hours, or less if the sulfur content of the oil is high. During this time the oil should be consumed at the rate of about 1 gram per hour.

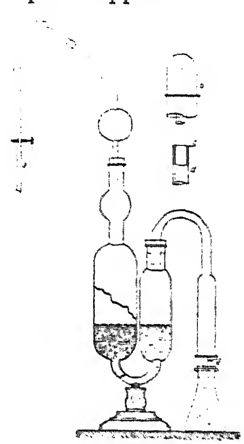


FIG. 161.—Apparatus for Determination of Sulfur in Oils. a, Suction tube; b, top of burner with glass cap in place; c, annealed top; d, part section of glass burner; e, glass burner.

Extinguish the flames and stop the suction on both absorbers. Weigh the oil lamp immediately and calculate by difference the weight of oil consumed. Working with the blank first, disconnect the spray trap and chimney and wash them thoroughly with the methyl orange solution, using a wash bottle with a very fine jet and collecting the washings in the absorber. The amount of solution required for washing should not exceed 35 cc. Carefully titrate the very faintly yellowish solution in the absorber with standard HCl, added to the suction side of the absorber from an accurately calibrated burette. During this titration the contents of the absorber should be agitated carefully, either by blowing through a rubber tube held between the operator's lips and connected at the other end with the chimney side of the absorber or else by the use of a suitable rubber syring bulb. As the end point is approached, draw the liquid back into the chimney

side between each addition of acid and then blow it into the suction side, agitating as before. As soon as the first permanent pink color appears the end point has been reached. Read and record the volume of HCl solution used.

Rinse the chimney and spray trap used in the actual determination into the absorber to which they were connected, exactly as prescribed for the blank. If the methyl orange solution in the absorber has a pink color, too much oil has been burned and the determination must be repeated, burning for a shorter time. Titrate just as in the blank, making sure that the absorber is cold. Read and record the volume of HCl solution required.

Calculate the sulfur content of the oil by substituting the proper values in the following formula:

$$\text{Percentage of sulfur} = \frac{(\text{HCl for blank, cc.} - \text{HCl for sample, cc.}) \times 0.1}{\text{grams of oil burned.}}$$

If blank is not run the formula is

$$\text{Percentage of sulfur} = \frac{(Na_2CO_3 \text{ cc.} - \text{HCl cc.}) \times 0.1}{\text{grams of oil burned.}}$$

These formulas are correct only for the standard solutions specified, 1 cc. of each being equivalent to 0.001 gram of sulfur. The use of solutions of other strength, such as N/10, involves more complicated calculations, and is not advisable.

It has been pointed out by Conradson that sulfonates and sulfates are left in the wick of the lamp since they are not volatil. A properly refined motor fuel should not contain these compounds, but there is no guarantee that they will not be found. S. Bowman [16] removes the wick, places it in a 6-inch length of combustion tubing, and connects it to the absorption bottle. The empty end of the combustion tube is heated gradually, moving the flame toward the wick, until the latter glows and finally burns to a light colored ash. If the heating is done in this manner the tarry matter is reduced to a minimum. The contents of the absorption bottle are poured into a 400 cc. beaker. All washings and the ash from the wick are added to the beaker as well. He then adds 1 gram of Na_2O_2, boils, acidifies with HNO_3 and precipitates the sulfate-ion with $Ba(NO_3)_2$. I should prefer to avoid the use of Na_2O_2 because this introduces more alkali metal salt. The oxidation can better be effected with bromine. The introduction of the gravimetric procedure increases the time required for the determination, but would in some instances be justified.

The Determination of Sulfur by Means of the Calorimetric Bomb.

The use of the calorimetric bomb for the determination of sulfur has been criticised because, (1) A small sample only can be taken, (2) it is difficult to wash all parts of the bomb, (3) of the possibility of incomplete combustion, (4) the lead gasket is attacked, (5) on account

[16] *J. Inst. Pet. Tech.*, 7 (1921), 334-8.

of the high temperature during combustion the products contain part of the sulfur as SO_2. In spite of these and other indictments, the use of the bomb for the determination of sulfur, particularly in the heavier oils, is common.

By proper manipulation most of these difficulties can be overcome. The best method of filling the bulbs, firing the charge, and handling the bomb is described under the determination of the heat of combustion of gasoline. Reference should be made to this section. Also a special-fitting and delivery-tube can be made so that the gases from the bomb can be bubbled through bromine water. In this way any SO_2 that may be formed will be oxidized and dissolved.

Sub-Committee VII of Committee D-2 of the A. S. T. M. has suggested a method for the determination of total sulfur in petroleum products by means of the bomb.[17]

The method (Method 520.3) of the Interdepartmental Petroleum Specifications Committee for sulfur in fuel oils is given below:

APPARATUS.

1. An oxygen bomb satisfying the following requirements:
(a) Capacity not less than 300 cc.
(b) Entire interior surface chemically resistant.
(c) Design and construction such that no leaks shall occur at any pressure or temperature generated during use, and such that when open, liquid contents can be easily and completely drained.

2. An oil-cup of platinum or glazed silica with a capacity not less than 2.5 or more than 5 cc.

3. Fuse-wire.—If platinum oil-cup is used, fuse-wire must be of platinum; if glazed silica oil-cup is used, fuse-wire may be of either platinum or iron. No. 35 B. & S. gage is a convenient size.

4. Accessories for bomb, such as oxygen supply, gage, charging connections, bench plate, wrench, bucket of water, and electrical connections.

5. Glassware and supplies.—Beakers from 300 to 500 cc. capacity; measuring graduates or pipettes; filtering funnels; hot plate or steam bath; crucibles and furnace suitable for ignition of precipitates; analytical balance sensitive to 0.0002 gram; "qualitative" filter paper, preferably 11-cm. size; "ashless quantitative" filter paper, capable of holding barium sulphate, preferable 9-cm. size (Whatman No. 42, S. and S., No. 589 Blue Ribbon, and A. D. Little are brands known to be satisfactory).

6. Reagents.—Distilled water. Sodium carbonate solution, containing 50 grams Na_2CO_3 per liter. Hydrochloric acid, c.p., sp.gr. 1.20. Bromine water (saturated). Barium chloride solution containing 100 grams of $BaCl_2.2H_2O$ per liter.

Note.—All reagents must be sulphur free.

[17] *Proc. Am. Soc. Test. Mat.*, 21 (1921), 365-6.

PROCEDURE.

7. Place from 10 to 20 cc. of distilled water in the bottom of the bomb. Place in the oil cup 0.6 to 0.8 gram of the oil to be tested and determine the weight of this charge to an accuracy of at least plus or minus 0.002 gram. Place the cup in the proper position in the bomb, arrange the ignition mechanism, and close the bomb. Admit oxygen slowly until a pressure of 40 atmospheres is reached. Attach leads from the firing circuit, place the bomb in a bucket of cold water. Open the valve of the bomb and allow the gas to escape, at an approximately even rate, so that the pressure is reduced to atmospheric in not less than one minute. Open the bomb and rinse all parts of its interior, including the oil-cup, with a fine jet of distilled water. Collect all washings, which should not amount to more than 350 cc., in a beaker. *Particular care must be taken not to lose, by splashing or otherwise, any of the liquid contents of the bomb.* Add 10 cc. of the sodium-carbonate solution to the washings, heat almost to boiling, and keep at this temperature for five minutes. Filter through a washed "qualitative" filter paper. Wash the filter thoroughly. Add 2 cc. of the concentrated HCl and 10 cc. of saturated bromine water to the filtrate. Evaporate to about 75 cc. on the steam bath or hot plate. To the hot solution add, in a fine stream or dropwise, 10 cc. of hot barium-chloride solution. Stir during the addition and for two minutes afterwards. Allow to stand overnight, or keep hot for one hour on the steam bath or hot plate, allowing the precipitate to settle for an hour while cooling. Filter the supernatent liquid through the "ashless quantitative" filter paper, wash the precipitate with hot water, first by decantation, then on the filter, till free from chloride. Transfer the paper and precipitate to a suitable crucible, dry at low heat until moisture is evaporated, char the paper (without flaming), and finally ignite at a good red heat until the precipitate is just burned white. A satisfactory means of accomplishing these operations is to place the crucible containing the wet filter paper in a cold electric muffle-furnace and turn on the current. Drying, charring, and ignition will usually occur at the desired rate.

After ignition is complete allow the crucible to cool to room temperature and weigh. The use of a dessicator is not recommended.

From the increase in weight of the crucible calculate the percentage of sulfur as follows:

$$\text{Percentage of sulfur} = \frac{\text{grams of } BaSO_4 \times 13.734}{\text{grams of oil used.}}$$

Elementary Analysis.

Routine work seldom calls for making elementary analyses, but these must frequently be made in investigational work. Precise results are obtained only by the most careful work. The space required for the presentation of methods for the determination of carbon, hydrogen, and nitrogen makes it impossible to include this subject matter here.

Reference should be made to Dr. Harry L. Fisher's excellent "Laboratory Manual of Organic Chemistry,"[18] part II of which (pp. 216-302) is devoted to this subject; and to Francis C. Benedict's "Elementary Organic Analysis—The Determination of Carbon and Hydrogen."[19] Both of these authors give numerous references to the original literature.

Heat of Combustion.

The heat of combustion of gasoline and similar volatil distillates can be accurately determined in the bomb calorimeter if the regular procedure is somewhat modified. The usual procedure is discussed in standard works on fuel analysis,[20] to which reference should be made. The technique that I have found to be satisfactory is essentially that of Richards and Jesse[21] and Richards and Barry.[22] The chief difficulty in determining the heat of combustion in the bomb is incomplete combustion. Gasoline is so volatil that it vaporizes faster than it can be burned, even though the combustion is very rapid. To obviate this difficulty a platinum crucible, about 2 cm. in diameter at the top and 2.5 cm. high, is substituted for the usual dish that holds the sample. The gasoline, contained in a thin-walled glass bulb, is placed in the bottom of this crucible. A disc of thin asbestos paper is then placed so that it rests on the bulb. A microscope cover-glass can be used for this purpose, but is not so easy to keep in place as the asbestos. In either case the disc should be notched at the edge in order to permit easy escape of the vapor. About 0.2 gram of pure sucrose, or 0.15 gram pure benzoic acid, is accurately weighed and placed on top of the asbestos or glass disc. The ignition wire is coiled and placed so that it ignites the sugar or benzoic acid. When the bomb is fired the heat from the burning sugar or benzoic acid causes the glass bulb to break, and the vapors of the gasoline or other volatil liquid are forced to pass through the zone of combustion. Complete combustion is thus assured. The bomb should always be examined for the odor of incompletely burned products, and for sooty deposits that indicate incomplete combustion. No correction for the asbestos or glass disc is necessary.

Careful attention must be given to several other manipulative details. The sample should weigh about 0.8 grams, and should be contained in a sealed thin-walled glass bulb just large enough to hold the sample. The sides of the bulb should be flattened so that such elasticity as the glass possesses is taken advantage of in order that the bulb will not break when placed under pressure. The usual method of filling the bulb is to warm it with the hand, or on a piece of warm metal, and then insert the capillary into the sample. As the bulb cools liquid is

[18] Pub. J. Wiley & Sons, 1920.

[19] Pub. Chemical Publishing Company, 1921.

[20] White, "Gas and Fuel Analysis." Sherman, "Organic Analysis." Gill, "Gas and Fuel Analysis for Engineers." Parr, "Fuel, Gas, Water, and Lubricants."

[21] *J. Am. Chem. Soc.*, 32 (1910), 284-5.

[22] *J. Am. Chem. Soc.*, 37 (1915), 1003-1020.

drawn in. This method is satisfactory when the sample is a single substance. However gasoline is a mixture, and there is loss of the more volatil components, and thus change in composition, when this procedure is used. The error is probably small and doubtless negligible in many instances. However, it can be easily avoided by the use of a thin-walled bulb with two capillary tubes. The sample can be quickly drawn into such a bulb, and a needle-point flame from a hand-torch can be used to seal off the capillaries. In any case the bulb must be filled as nearly full as is possible, for otherwise it will break when pressure is applied to the bomb.

Best results will be obtained if oxygen is admitted to the bomb until the pressure is 20 to 22 atmospheres. Higher pressures often break the glass sample-capsules. Richards and Barry have found that at pressures of 30 or more atmospheres odoriferous gaseous products are formed. One cc. of water should be introduced into the bomb before it is closed. This is more than enough to saturate the air with water vapor, and thus cause complete condensation of all water formed during combustion. Richards and Barry used a pure soft gold gasket in place of the ordinary lead one that they found was too easily attacked. The gold gasket is particularly suitable if sulfur is to be determined.

The original papers of Richards should be consulted if it is desired to introduce more finesse into the combustion procedure. As an example of the accuracy attainable it may be noted in passing that Richards and Barry's greatest variation from the mean heat of combustion of benzene was 0.04 per cent.

Vapor-Pressure.

The method specified by the Bureau of Explosives for determining the vapor-pressure of volatil inflammable products such as natural-gas gasoline is given below. For information and methods for accurately determining the vapor-pressure of substances, and mixtures of substances, the original literature must be consulted.

Bureau of Explosives' Method.

APPARATUS.

The apparatus shown in Figure 162 consists of an iron or steel pipe, of two-inch size, with caps screwed on the ends. The upper cap has a ¼-inch nipple screwed in, and is connected by a coupling to a 3-in., 30-lb. pressure-gage. The gage is known as the Inspectors Gas Gage and is made by the Pittsburgh Gage & Supply Co. All joints must be entirely tight. Joints between the large pipe and caps are best sealed with solder. Approximate external dimensions are indicated on the sketch. In addition, a 12-in. by 3-in. tin cylinder is required for filling the apparatus. The tin cylinder is provided with a lip for pouring. A small tin cover ¾ in. deep fitting over bottom of tin cylinder may be removed and used for measuring one-tenth the capacity of the

apparatus. A tin funnel 2½ in. in diameter, with a stem 3 in. long and 3/16 in. in diameter should be used in filling the apparatus. In addition, a pressure gage, a water-bath for heating, and a thermometer are required.

PROCEDURE.

Remove the gage from the tube, and fill the tube to 90 per cent of its capacity by lowering it into the storage-tank, in an upright position, by means of a cord or wire. Leave the tube immersed for several minutes, then withdraw it and pour off liquid until the tube contains 90 per cent of its capacity. The measure having a capacity of 10 per cent of the tube should be used for this purpose.

In case it is impracticable to lower the tube into the storage tank, draw the liquid off into a vessel of a capacity about equal to that of the tube. Pour the liquid into the tube until it is about half-filled. Shake the tube and its contents gently in order to bring both to the same temperature. After standing for several minutes, pour all of the liquid out of the tube. Then draw another sample from the storage tank into the cylinder, and pour it through the funnel into the tube until the latter is entirely filled. Withdraw 1/10 as before. Screw the gage tightly into position, using a little liquid shellac on the joint to insure tight closure.

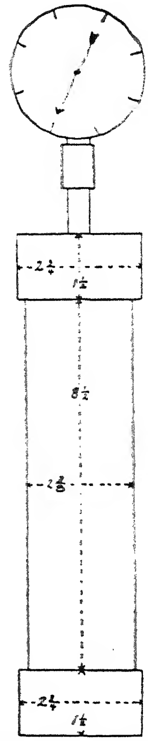


FIG. 162.—Apparatus for Determining "Vapor-Pressure."

Immerse the tube in water at 70° F., and allow it to remain for five minutes (the water should be stirred constantly). Remove the tube from the water, and unscrew the gage sufficiently to relieve the pressure indicated by the gage. At the expiration of a 20-second interval screw the gage tightly into place again. Place the tube in water at a temperature of 100° F. (90° F. from Nov. 1 to March 1). The level of the water must be just below the lower edge of the pressure gage. Stir the water continually, and maintain the temperature exactly constant for ten minutes, then tap the gage lightly with the fingers and read the pressure.

A correction of pressure figures should be made according to the initial temperature of the gasoline as follows:

For tests on samples taken at a temperature of 50 to 59° F., deduct 1 pound.

For tests on samples taken at a temperature of 40 to 49° F., deduct 2 pounds.

For tests on samples taken at temperatures below 40° F., deduct 3 pounds.

In making reports, the gravity of the liquid, the temperature of the liquid as placed in the tube, the pressure at 70° F., before venting the tube, and the corrected pressure at 100° F. (90° F. from Nov. 1 to March 1) after venting 70° F., should be recorded.

Viscosity.

The viscosity of gasoline cannot be measured by the use of the Saybolt Universal, Engler, or Redwood viscosimeters since the efflux tubes of these instruments are so large in diameter and so short that the flow of gasoline through them is not viscous but turbulent. The Ubbelohde instrument is used in Europe. This instrument and its use is described by W. H. Herschel in Technologic Paper No. 125 [23] of the U. S. Bureau of Standards, to which reference should be made. Viscosities should be expressed in absolute units, that is, either in poises or centipoises. The reader should refer to the discussion of viscosity in Chapter V on fluid flow. The recent book by E. C. Bingham on "Fluidity and Plasticity" will also be found a copious source of reference material. The type of viscosimeter used by Kendall and Monroe [24] will be found useful in research work.

The Saybolt Thermo Viscosimeter is used to some extent in this country. This instrument and the method of using it are described by H. T. Bennett [25] from which the following is quoted. The letters refer to Figure 163.

"The sample, freed from sediment and moisture, is poured into the cylinder V, leaving, however, enough room for the displacement of the twin-tubes (L) when immersed in the oil. The tubes (L) are then placed in the cylinder and left there until a uniform temperature throughout the oil has been attained. If necessary, the tubes are moved up and down to obtain a uniform mixture.

"When the temperature is constant attach rubber tubing (N) on the Woulff bottle (R) to the long leg (K) of the siphon, and draw off the surplus oil until the oil level reaches the upper mark (D) on the long capillary tube. The oil level and the upper mark must always coincide when making a test in order to preserve the same constant-head level for all tests.

"Attach (B) to the top of capillary tube (C), as shown, so that it will firmly rest on hanger plate (H). With the forefinger closing the air hole (A) in compression bulb (B) on the capillary tube, gently and slowly press the bulb with thumb and middle finger until the capillary tube (C) is entirely emptied, an indication of which is a steady stream of air bubbles (indicated by G) ascending through the oil in cylinder (V).

"Hold a stop watch in left hand and, while air bubbles are still ascending, gently slip the forefinger up and off the air hole in bulb (B),

[23] Obtainable from the Superintendent of Documents, Washington, D. C., for five cents.

[24] *J. Am. Chem. Soc.*, 39 (1917), 1787-1802.

[25] *Pet. Age*, Dec. 15th, 1921, 26-7.

simultaneously starting the watch. The adding and removing of the pressure on the bulb (B) must be so gentle as to prevent the possibility of the column of oil in capillary tube (C) being broken. Should this occur, simply force out the column slowly, and start anew.

"After the pressure is released, the oil will ascend the capillary tube (C). The instant that the top of the oil column reaches the mark (E), stop the watch and mark down the reading. The decimal part of a second is counted as a unit. The temperature indication shown on the

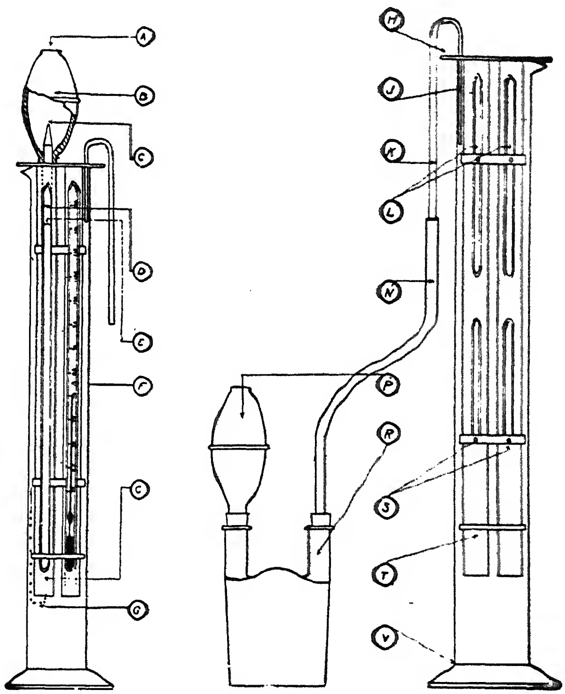


FIG. 163.—Saybolt Thermo-Viscosimeter.

thermometer (F) is noted. The test is repeated three or more times to insure against personal errors. The viscosity corrected to 60° F. is then ascertained by consulting the temperature correction chart furnished with each instrument."

Mr. Bennett objects to the Saybolt Thermo-Viscosimeter in its present form because it is easily tipped over, and because the capillary tube and thermometer must be removed from the test jar after each experiment. These fragile parts are easily broken. He suggests a modified form of the instrument shown in Figure 164. The base of the test jar was cut off and sealed into a tin container A that may be com-

pletely emptied by means of stop-cock B. The glass jar and tin container were cemented together with a mixture of waterglass, litharge, and glycerine. The tin container was attached to a wooden base loaded with lead to render it less easily tipped. In using the instrument the oil is poured into the apparatus through a funnel inserted in a hole in the metal disc that supports the capillary tube. The excess oil is then drained from the stop-cock. The capillary tubes used were 0.1 mm. inside diameter, and 318 mm. long from the tip of the capillary. Results of 65 tests on a 500-viscosity kerosene were found to agree within ± 5. Mid-Continent 56 to 61° Bé. gasolines were found to have viscosities ranging from 125 to 154, and 40 to 43° Bé. kerosenes from 320 to 545.

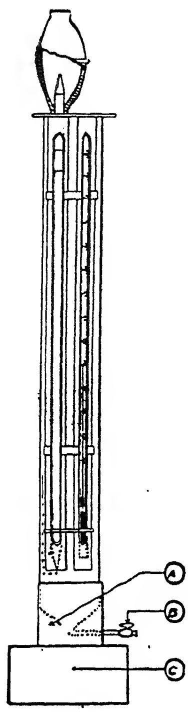


FIG. 164. — Modified Saybolt Thermo-Viscosimeter.

Determination of Unsaturation.

The broadening use of cracking processes necessitates the development of methods for estimating the proportion of unsaturated compounds in gasoline or other motor fuels. The difficulty in the use of these olefinic products arises probably from their content of di-olefinic or isomeric hydrocarbons, that readily polymerize and oxidize with formation of gummy substances. Real knowledge of this entire subject is at present very limited. The most comprehensive discussion of the olefins and their reactions is that of Brooks and Humphrey[25a] to which reference should be made.

At present no method is in use that determines the volumetric percentage of olefins in hydrocarbon mixtures. The volumetric methods now in use give empirical results that are taken as a guide to the olefin content, and the result is given as per cent "unsaturation."

Sulfuric Acid Method of the Interdept. Pet. Spec. Comm. for Unsaturation in Gasoline. (Method 550.1.)

APPARATUS.

The graduated portion of the neck of the special Babcock bottle shall contain 10 cc. (± 0.05 cc.) at a temperature of 20° C. and shall be graduated in 2 per cent divisions and numbered every 10 per cent from the bottom up, the first and each succeeding 10 per cent line to be longer than the others.

[25a] *J. Am. Chem. Soc.*, 40 (1918), 822-56.

2. A pipette, calibrated to deliver 10 cc. (± 0.05 cc.) of aviation gasoline at a temperature of 20° C.

3. A 20-cc. graduate.

MAKING OF TEST.

With the pipette place 10 cc. of the gasoline to be tested in a clean, dry unsaturation test bottle, cool for two minutes by immersing in ice water, then add 20 cc. of commercial 66° sulfuric acid (containing approximately 93.2 per cent H_2SO_4) from the graduate. Care should be taken that the acid runs quietly down the side of the bottle instead of splashing onto the surface of the gasoline. Close the bottle with a rubber stopper and shake, first slowly, then vigorously with a rotary motion for five minutes. Separate the gasoline and the acid by either of the following methods:

Gravity separation.—Add sulfuric acid to the contents of the bottle until the surface of the liquid is level with the upper graduation mark on the neck. Stopper tightly and allow the bottle and contents to stand 12 hours. Report the percentage loss of volume of the gasoline as percentage of unsaturation.

Centrifugal separation.—Place the stoppered bottle in a suitable centrifuge and whirl it for two or three minutes at a speed of 500 to 1,000 revolutions per minute. Add sulfuric acid until the surface of the liquid is level with the lower graduation mark and again centrifuge. Add acid to bring the liquid to the upper graduation mark, and report the unsaturation as above.

Comments on Sulfuric Acid Method.

Dean and Hill[26] refer to the sulfuric acid method as "rapid, reliable, and of fair accuracy." I can agree with this only if it is understood that the test is highly empirical. The chemical reactions of even apparently similar olefins are often so different that one would not necessarily expect a broadside attack on complex mixtures of olefins to give comparable results. When olefins are treated with sulfuric acid, at least four reactions are involved: (1) Formation of mono- and di-alkyl sulfates, (2) Alcoholization, (3) Polymerization, (4) Oxidation. The net result depends on the nature of the olefins, the strength of the H_2SO_4, the temperature, and the time involved.

I have found[27] that sulfuric acid containing 87 to 88 per cent H_2SO_4 by weight causes the largest volumetric loss from hydrocarbon mixtures containing olefins.

As the acid strength increases from 88 per cent, the effect is to cause increasingly rapid polymerization of the olefins. Acids stronger than 95 per cent H_2SO_4 remove saturated hydrocarbons as well as olefins. Sulfuric acid, containing 12.7 per cent excess SO_3, removed

[26] U. S. Bur. Mines, Tech. Paper 181.

[27] Work (unpublished at this writing) carried out under my general direction by Mr. John C. Geneisse assisted by Mr. Arthur Good.

10 per cent by volume of a Pennsylvania kerosene, and 40 per cent by volume of a Mid-Continent kerosene, both of which had been treated for removal of olefins, and which showed no loss to sulfuric acid of 87 to 93 per cent strength.

The volumetric loss to sulfuric acid should be read immediately after centrifuging. If the bottles are allowed to stand, the volume of residual oil increases. This is particularly true when sulfuric acid of 85 to 93 per cent strength is used. In view of this fact it is evident that quick separation of oil and acid by centrifugal force is essential to the obtaining of correct results.

Determination of the "Olefin Number."

Determination of the volumetric loss to sulfuric acid is a rapid method of obtaining empirical information useful in plant control. However, in purchasing gasoline, one desires to know whether the product will cause trouble, either in storage or in use, through oxidation or formation of gummy deposits. This is probably more a question of the nature of the olefins than of the quantity contained in the gasoline. I have found the determination of what I have chosen to call the "olefin number" useful in judging the quality of gasolines containing unsaturated hydrocarbons. The test is carried out as follows:

A quantity of the gasoline, sufficient to yield somewhat over 100 cc. of residual oil, is treated at 0° C. with 2.5 volumes of 1.84 sp. gr. sulfuric acid. The acid is added as rapidly as is possible without allowing the temperature to rise above 5° C. When all of the acid has been added, the reaction mixture is well shaken for five minutes. The temperature is not allowed to rise during this period. The reaction mixture is then poured into the cups of a large centrifuge, and the oil and acid separated quickly but completely. 100 cc. of the residual oil is then distilled in accordance with the standard method for gasoline. The distillation curves of the gasoline, and of the residual oil, are then plotted on accurate cross-section paper. The "olefin number" is obtained by adding together the ordinate differences, in Fahrenheit degrees, between the two curves at each 5 per cent abscissa interval, and dividing by the total number of ordinate differences summed. It will be noted that when the temperature rises to 680 to 700° F., cracking starts, and the curve bends downward. High boiling polymers have been formed, and the gasoline should be penalized accordingly. To effect this, ignore the drop in the distillation curve, and project it up and to the right in the direction indicated by the curvature to the left of the break in the curve. In this manner an ordinate difference corresponding to 95 per cent distilled is obtained.

Olefin numbers ranging from practically 0 up to 200 have been [illegible] Duplicate determinations have been found to check very [illegible] etermination gives a good picture of the polymerizing [illegible] e gasoline. A planimeter can be used to facilitate the

Iodine and Bromine Numbers.

The usefulness of iodine numbers as an aid in the identification of oils and fats has led to studies of iodine numbers of unsaturated gasoline, and other petroleum products, in the hope that their determination would be an accurate measure of unsaturation. Results so far obtained are somewhat conflicting, but in general indicate that iodine numbers are not a measure of unsaturation. The recent paper of W. F. Faragher, W. A. Gruse, and F. H. Garner,[28] and that of E. M. Johansen[29] should be consulted. Both contain much valuable original work, and, in addition, the first gives many references, and the second a bibliography of 29 titles.

Some olefins add iodine almost quantitatively, as shown by Faragher et al, but this is apparently not true of all. Johansen concludes that iodine numbers are not indicative of the unsaturation of petroleum products, because substitution of iodine for hydrogen, as well as addition of iodine to double bonds, occurs.

Development of an Organic Technique.

One of the most useful services that could be rendered the oil industry would be the development of a reliable organic technique that would enable one quantitatively to determine the components of hydrocarbon mixtures. The lack of knowledge such as this has greatly retarded the progress of petroleum technology. Much work is done, and published under the guise of that pretty fiction "petroleum chemistry," that is in reality highly empirical. One starts with a mixture of he knows not what, and ends up with another, but different, mixture of the same sort.

Valuable fundamental information is to be found scattered through the technical literature of petroleum. The task of gathering this together, and correlating it, is a very large one, and one that could only be satisfactorily done if the process included a great deal of supplementary laboratory work. The publication of Brook's work, "The Non-Benzenoid Hydrocarbons," and of the tables of hydrocarbon properties as a part of Day's "Handbook of the Petroleum Industry," should be of the greatest help in furthering the development of a comprehensive organic technique that would sooner or later be published as a handbook of laboratory technique. Petroleum chemistry is so specialized a field that the puerile treatments of the subject in the standard reference works of organic chemistry are little more than amusing. The need is definite, and the job is a big one,—so large in fact that the industry cannot expect to see it thoroughly and properly done except by an organization that is subsidized for the purpose in a substantial manner. The valuable results that should accrue from such work would be of benefit to all, and the burden of expense should be

[28] *J. Ind. Eng. Chem.*, 13 (1921), 1044.
[29] *J. Ind. Eng. Chem.*, 14 (1922), 288.

borne by all. Clearly it is a task to be handled by organized and co-operative effort.

In the absence of a comprehensive treatise the only recourse is to make reference to the writings of such investigators as Mabery, Engler, Markownikow, Marcusson, Edeleanu, Konowaloff, Chavanne, Tausz, Brooks, Armstrong, and others, and to such information as is contained in the standard reference works of petroleum technology and organic chemistry. Engler-Hofer's "Das Erdol" is particularly to be recommended. It is to be regretted that we, in this country, have not made more fundamental contributions to petroleum chemistry. We have been "skimming the cream," but deserve to be made to get down to business on the "curds and whey."

Fire Protection in the Laboratory.

It is to be assumed that any laboratory handling volatil inflammable liquids is equipped with suitable fire extinguishers of the foamite-fire-foam type.

A useful addition to the usual equipment of such laboratories is described by L. S. Bushnell.[30] The usefulness of a woolen blanket to smother flames is well known. The accessibility of the blanket in time of need is most important. Bushnell's blanket holder consists of a triangular box, hinged to the ceiling, and held closed by a spring catch, which, when released by jerking a cord, allows the box to fall open and swing back, and the blanket to drop out, unroll, and hang ready for use. The device should commend itself to refinery laboratory men.

REFERENCE WORKS

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Gill, "Gas and Fuel Analysis for Engineers."
Holde-Mueller, "Examination of Hydrocarbon Oils and Saponifiable Fats."
Kissling, "Laboratoriumsbuch für die Erdolindustrie."
Leach, "Food Inspection and Analysis."
Lewkowitsch, "Technology of Oils, Fats and Waxes."
Lunge-Berl, "Chemisch-Techische Untersuchungs-Methoden."
Ostwald-Luther, "Hand-und Hülfsbrich zur Ausfuhrung Physiko-Chemischer Messungen."
Parr, "Fuels, Gas, Oils, and Water."
Rakusin, "Die Untersuchung des Erdöles und Seiner Produkte."
Redwood, "A Treatise on Petroleum."
Sherman, "Organic Analysis."
White, "Gas and Fuel Analysis."

[30] *J. Ind. Eng. Chem.*, 13 (1921), 1081.

Chapter XVII.

Useful Physical Data and Tables.

The subject matter of this chapter consists of information useful to the producer or user of motor fuels. It is largely presented in tabular form. Limited explanatory notes are added or included where necessary or desirable. I have made no effort to include such matter as often comprises a large part of the Appendix of many books, or which is to be found in the standard handbooks or compilations of physical and chemical constants.

Properties of the Crude Oils of the United States.

The U. S. Bureau of Mines has issued several publications dealing with the properties of the crude oils of the United States. Specific gravities, percentages of sulfur, percentages of water, distillation data at ordinary pressure and under a vacuum, and Conradson carbon residue percentages are given. These reports are too voluminous and detailed to be reproduced here. Nor is this necessary, for they are easily available to all that are interested. The reports so far issued are:

Serial No. 2202, "Properties of Typical Crude Oils from the Eastern Producing Fields of the United States," by E. W. Dean, January, 1921.

Serial No. 2235, "Properties of Typical Crude Oils from the Producing Fields of the Rocky Mountain District," by E. W. Dean, M. B. Cooke, and A. D. Bauer, April, 1921.

Serial No. 2290, "Viscosities and Pour Tests of Typical Crude Oils from the Eastern and Rocky Mountain Producing Fields of the United States," by E. W. Dean, A. D. Bauer, and W. B. Lerch, October, 1921.

Serial No. 2293, "Properties of Typical Crude Oils from the Producing Fields of Northern Texas, Northern Louisiana, and Arkansas," by E. W. Dean, M. B. Cooke, and C. R. Bopp, November, 1921.

Serial No. 2322, "Properties of Typical Crude Oils from the Producing Fields of Kansas," by E. W. Dean, M. B. Cooke, and A. D. Bauer, February, 1922.

Serial No. 2364, "Properties of Typical Crude Oils from the Producing Fields of Oklahoma," by E. W. Dean, A. D. Bauer, M. B. Cooke, and C. R. Bopp, June, 1922.

TABLE LXXXI

SOURCES AND PHYSICAL CONSTANTS OF CRUDE OIL SAMPLES

No.	Field	District	Sampled	Location	State	County	Lease	Well No.
269	Cal.	Piru	12/ 6/07	T3N, R18W	Cal.	Ventura	Union Oil Co.	15
273	Cal.	Piru	12/ 4/07	T4N, R18W	Cal.	Ventura	Modella, 7, 19, 21, 22, 28, 29	..
587	Cal.	Midway	10/ 8/10	T31S, R22E	Cal.	Kern	Manchuria, Midway	1
591	Cal.	Midway	10/18/10	T31S, R22E	Cal.	Kern	Bear Creek	3
Heald								
764	Pa.	J. S. Sloan	9/ 7/11	Emlenton	Pa.	Venango	Boulder Sand: 1195 ft.	9
765	Pa.	Farm	9/ 7/11	Emlenton	Pa.	Venango	Second Sand: 1050 ft.	3
815	Pa.	Branden	9/21/11	Pleasantville	Pa.	......	First Sand: 580 ft.	11
816	Pa.	Farm	9/21/11	Pleasantville	Pa.	......	Second Sand: 650 ft.	6
1280	Okla.	Collinsville	May/13	T22N, R15E	Okla.	......	Claremore Pool	..
1281	Okla.	Collinsville	May/13	T22N, R15E	Okla.	......	Sellers Lease, Claremore Pool	1
1336	Okla.	Collinsville	5/24/13	T14N, R18E	Okla.	......	G. Callahan Lease, Muskogee Pool	3
1339	Okla.	Collinsville	5/24/13	T14N, R18E	Okla.	......	Stevens Lease, Muskogee Pool	1

S. Maria
R. R. Russian—Provided by the kindness of C. I. Robinson of the Standard Oil Co. of N. J.
R. M. Russian—Provided by the kindness of Prof. C. F. Mabery, The Case School, Cleveland, O.
Mex. Mexican—Provided by the kindness of Dr. D. T. Day, U. S. Bureau of Mines, Washington, D. C.

Physical Constants of Crude Petroleums Arranged in Order of Their Specific Gravities

Sample	Sp. Gr.	Viscosities Spec.	Viscosities Sec.	Surf. Tens.	Cap. C'nst
815	0.799	1.30	67.5	24.07	6.17
764	0.800	1.29	67	25.12	6.44
816	0.808	1.32	68.5	24.81	6.30
765	0.816	1.40	73	25.44	6.38
1336	0.825	1.44	75	24.78	6.15
1339	0.838	1.71	89	26.19	6.40
1280	0.846	1.70	88.5	25.03	6.06
Heald	0.865	2.77	144	26.59	6.30
1281	0.870	3.35	174	26.59	6.26
269	0.876	2.31	120	25.70	6.00
R. R.	0.876	2.61	136	27.55	6.43
R. M.	0.878	3.22	167.5	27.82	6.49
273	0.891	2.11	110	26.08	5.99
S. M.	0.901	4.92	256	26.13	5.94

Relationships between the Physical Constants of Petroleum Distillates.

The following tables and data are taken from an article by Rittman and Dean.[1] The context and tables are reproduced exactly as in their article.

For the purpose of determining possible simple relationships, measurements were made of the following series of constants:

A—Distillation range
B—Specific gravity
C—Refractive index
D—Viscosity
E—Surface tension
F—Capillary constant
G—Molecular weight
H—Ultimate analysis

SAMPLES AND DETERMINATIONS.

As the present work deals with a comparison of constants, rather than oils, it was not considered necessary to secure an absolutely comprehensive series of samples. Representative oils from a number of different fields were obtained, and the selection was made with the view of including crude petroleums of different types.

The list includes five carefully selected samples of California crude oils, five from Oklahoma, four from Pennsylvania, two from Russia and one from Mexico. From the works of Mabery and other investigators, it is known that wide differences exist among the types of hydrocarbons found in oils from the different fields. Table LXXXI gives the sources and physical constants of the oils studied.

Viscosities of the crude oils were measured in the Standard Engler Viscosimeter at a temperature of 20° C. Results are expressed in Engler degrees, which represent ratios of the rates of flow of the oil and water.

Distillations were conducted according to a method which was designed to give a high degree of separation. In accordance with the results of some recent investigations conducted under the direction of one of the authors, a Hempel column of definite height was provisionally adopted as standard for this set of experiments. The degree of efficiency attained was approximately that of the standard creosote flask of the Forestry Division of the Department of Agriculture. The flasks here used were of the following dimensions:

Initial charge	400 cc.	Height from bulb to outlet 6 in.
Capacity of bulb............	500 cc.	Height from outlet to top 1½ in.
Cuts at 50° intervals..........	100 to 300° C.	Diameter of neck of bulb ⅝ in.
Fractionating column: 5 in. aluminum beads		(between ¼ and ⅜ in.).

The results of distillation, shown in Table LXXXII need no discussion in the present connection. The Kern River and Mexican Oils were emulsified and frothed badly, and to overcome this difficulty it

[1] *J. Ind. Eng. Chem.*, *7* (1915), 578-82.

TABLE LXXXII

RESULTS OF FRACTIONAL DISTILLATIONS OF PETROLEUM OILS, AND CONSTANTS OF VARIOUS DISTILLATION CUTS

Source....	Cal.	Cal.	Cal.	Cal.	Cal.	Pa.	Pa.	Pa.	Pa.	Okla.	Okla.	Okla.	Okla.	Okla.	Russian		Mexi-
Sample....	269	273	587	591	S. M.	764	765	815	816	1280	1281	1336	1339	Heald	R. R.	R. M.	can
VOLUME—PERCENTAGES																	
To 100°	8.00	5.25	0.38	...	6.75	5.19	6.25	6.25	8.25	3.25	0.31	8.38	5.50	5.00	0.62	1.12	...
100–150°	10.50	15.50	0.50	...	13.25	7.38	13.75	6.63	14.25	14.25	3.38	12.50	12.25	8.62	11.13	7.38	1.12
150–200°	8.25	10.25	1.50	1.25	8.62	6.06	11.50	6.00	12.75	10.38	10.75	11.12	9.50	7.38	11.50	8.62	2.50
200–250°	11.00	12.63	5.25	5.25	11.12	6.12	11.50	5.25	11.75	13.88	14.12	11.12	11.75	10.25	13.75	12.75	8.25
250–300°	11.25	12.00	16.00	10.63	15.00	6.19	12.50	5.75	11.75	14.88	16.75	12.63	15.00	17.00	15.25	15.62	25.75
SPECIFIC GRAVITIES																	
To 100°	0.688	0.706	...	...	0.706	0.686	0.682	0.671	0.686	0.705	...	0.680	0.689	0.690	...	0.733	...
100–150°	0.756	0.762	...	...	0.762	0.736	0.748	0.737	0.740	0.746	0.757	0.749	0.752	0.754	0.767	0.769	0.759
150–200°	0.792	0.805	0.820	0.826	0.806	0.766	0.780	0.767	0.771	0.781	0.785	0.783	0.785	0.791	0.804	0.806	0.798
200–250°	0.825	0.851	0.858	0.860	0.846	0.789	0.799	0.792	0.793	0.814	0.815	0.809	0.812	0.818	0.836	0.836	0.843
250–300°	0.855	0.891	0.887	0.890	0.878	0.812	0.818	0.815	0.813	0.839	0.839	0.831	0.836	0.839	0.861	0.861	0.871
INDICES OF REFRACTION																	
To 100°	1.386	1.390	1.423	...	1.392	1.385	1.385	1.375	1.386	1.389	1.409	1.385	1.387	1.388	1.401	1.403	...
100–150°	1.418	1.419	1.434	...	1.420	1.407	1.416	1.408	1.410	1.413	1.419	1.416	1.417	1.418	1.421	1.423	1.419
150–200°	1.436	1.440	1.445	1.448	1.444	1.425	1.430	1.426	1.427	1.431	1.435	1.432	1.434	1.435	1.439	1.441	1.439
200–250°	1.455	1.465	1.465	1.465	1.465	1.437	1.443	1.438	1.439	1.449	1.450	1.448	1.448	1.451	1.457	1.457	1.464
250–300°	1.472	1.493	1.484	1.484	1.483	1.449	1.452	1.449	1.449	1.464	1.464	1.459	1.461	1.465	1.472	1.474	1.481
SURFACE TENSIONS																	
To 100°	19.54	18.92	...	...	20.78	18.81	18.87	19.11	19.53	19.99	...	19.85	18.92	19.71	...	21.19	...
100–150°	22.12	22.33	...	...	22.47	20.95	21.87	21.67	20.98	22.05	22.69	22.09	21.53	22.34	22.75	22.80	...
150–200°	22.70	24.55	25.25	25.36	25.31	23.29	24.00	23.75	22.64	24.25	24.35	24.07	22.91	23.98	24.85	24.93	24.62
200–250°	23.47	26.43	28.62	27.22	26.28	25.04	25.29	25.42	23.67	26.13	26.12	25.61	23.91	24.99	26.50	26.71	26.36
250–300°	23.81	28.18	29.51	28.03	28.04	26.47	26.84	26.80	24.48	27.48	27.37	27.02	24.45	26.01	27.15	28.01	27.26
CAPILLARY CONSTANTS OR SPECIFIC COHESIONS																	
To 100°	5.84	5.50	...	...	6.04	5.64	5.69	5.86	5.84	5.82	...	6.00	5.64	5.86	...	5.93	...
100–150°	6.00	6.01	...	...	6.06	5.84	6.13	6.03	5.81	6.06	6.15	6.05	5.88	6.07	6.08	6.08	...
150–200°	5.87	6.25	6.30	6.29	6.44	6.23	6.46	6.35	6.02	6.32	6.36	6.31	5.99	6.21	6.34	6.34	6.33
200–250°	5.82	6.36	6.83	6.48	6.36	6.51	6.61	6.58	6.12	6.57	6.56	6.49	6.03	6.26	6.49	6.55	6.39
250–300°	5.71	6.47	6.81	6.45	6.54	6.68	6.79	6.73	6.16	6.71	6.68	6.66	5.99	6.34	6.46	6.67	6.41
CRYOSCOPIC MOLECULAR WEIGHTS																	
150–200°	133.3	125.8	131.4	142.9	125.9	137.6	121.7	139.8	130.3	132.2	138.3	130.6	130.7	127.8	127.6	119.1	142.7
200–250°	166.7	152.7	151.5	179.2	140.0	164.5	159.4	167.3	149.0	158.4	170.1	165.9	153.9	159.8	146.4	140.7	178.3
250–300°	191.6	173.2	181.8	193.9	179.6	202.6	184.2	205.8	180.9	195.7	212.3	214.3	190.6	192.5	171.3	180.5	197.7

was necessary to apply heat to the neck of the flask, which obviously altered the effect of the fractionating column.

Specific gravity determinations were made at 15° C. by the use of a special small Westphal Balance with a plummet of 1 cc. displacement.

A study of the specific gravities shown in Table LXXXII brings out one fact, which, though well known, is worthy of comment. If for any given temperature a cut is selected, it will be noted that densities of Pennsylvania products are least and those of California and Russian greatest. This is in accord with observations of other investigators and is a striking evidence of the difference among the hydrocarbons contained in petroleums from different fields. Pennsylvania oils contain paraffins which have a low gravity for a given boiling point: California and Russian oils contain cyclic compounds which are heavier for the same boiling point: Oklahoma oils, containing both types of hydrocarbons, give intermediate gravity values.

Refractive indices were measured by means of a Pulfrich Refractometer. Determinations were made at room temperature, maintained at 20° C.

The use of refractive index as a means of identification of oils is to be recommended. The method is simple, rapid, and only a few drops of liquid are necessary for a determination. Comparatively little has been done in the use of refractive index by petroleum technologists, despite its wide utility in identifying essential oils. The property is an additive one and within certain limits we can assign to each atom in the molecule a certain share in the refractive index of the molecule.

The above property is emphasized by the present experiments. The values increase in the ascending order with increase of specific gravity of a series of oils: this is clearly shown when the oil is graphed against specific gravity and refractive index.

Surface Tension.—Up to the time of beginning this research but little attention has been given to the determination of surface tension and capillary constants of petroleum and its products. This phenomenon is important to the geologist[2] as well as to the chemist.

Surface tension is a direct result of unbalanced inter-molecular forces at the boundary between the liquid and gas phase, and is manifested by the apparent formation of an elastic skin. The familiar experiment of floating a greasy steel needle on water is the simplest and most impressive way of demonstrating the existence of a tension along the surface of a liquid. Two common resulting effects are the tendency of all liquids to form spherical drops whenever possible and the rise in tubes of all liquids which are able to wet the material of which the tube is composed.

Surface tension measurements were made by the use of the Morgan[3] drop weight apparatus. The method evolved by Morgan[4] and his co-workers is simple, rapid and highly accurate. It has in addition the

[2] *Bull. Am. Inst. Min. Eng.*, 1914, 2365.
[3] *J. Am. Chem. Soc.*, 32 (1911), 349.
[4] *Z. physik. Chem.*, 1915; *Jour. Am. Chem. Soc.*, 1911-1915 (résumé).

advantage of being particularly adapted to liquids which are mixtures of several constituents of different volatilities—whereas the capillary rise method fails utterly under these conditions.

The method gives directly and accurately the weight of the drop of the liquid. From this the value of surface tension can be calculated by the following relation.[5]

γ = Surface Tension (dynes per cm.) = KW where K = The constant for the apparatus used and W = Weight of a drop in milligrams.

It will be noted from the results shown in Table LXXXII that surface tension is apparently an additive property as far as the distillation cuts of any one oil are concerned, but that additivity vanishes when the relations of different petroleums are considered. An explanation is not difficult to find, for it has been demonstrated by Morgan [6] that small additions of certain substances influence greatly the surface tension of a solvent. Thus in the presence of 1 per cent of amyl alcohol the surface tension of water decreases 48 per cent, while 1 per cent of phenol [7] in water produces a 17 per cent depression of surface tension.

All this indicates the possible occurrence in crude petroleum of small quantities of substances which have a large influence on surface tension and which are distributed throughout the various cuts of a distillation. On this basis it is easy to understand why the apparent additive nature of this constant vanishes when relations of different original oils are considered. With pure hydrocarbons, of homologous series, surface tension is an additive property.

That phenols, cresols, mercaptans and other sulfur and oxygen compounds exist in crude petroleums has been clearly shown by the work of Markownikoff and Ogloblin,[8] Pebal and Freund,[9] Hall,[10] Thiele,[11] and Mabery.[12]

The above mentioned observations on surface tension have indicated interesting possibilities for research. It is hoped that in the near future investigations along these lines may be conducted and knowledge of more specific character obtained.

Capillary Constant or Specific Cohesion.—The capillary constant is a derived function of surface tension and specific gravity. It has been largely used in the past and many values in the literature are expressed in terms of this constant. For purposes of comparison the surface tension values obtained by the drop weight method have been converted into capillary constants. Transformations were made by the use of the following formula: [13]

[5] *J. Am. Chem. Soc.*, 33 (1911), 658.
[6] *Ibid.*, 35 (1913), 1860.
[7] Results on phenol not published—Morgan and Egloff.
[8] *Ber.*, 16 (1883), 1873; *Chem. Ztg.*, 1881, 609.
[9] Liebig's *Ann.*, 115 (1860), 19.
[10] *J. Soc. Chem. Ind.*, 1907, 1223.
[11] *Chem. Ztg.*, 175 (1901), 433.
[12] *Proc. Am. Acad.*, 36 (1901), 255; 40 (1904), 348.
[13] Morgan, "Principles of Physical Chemistry," 1914, 100.

$$\alpha^2 = \frac{2\gamma}{9.8d}$$

α^2 = Capillary Constant γ = Surface Tension d = Specific Gravity

Values of d for 20° were calculated (see Table LXXXII) from those measured at 15° by conversion figures given by Markownikoff-Ogloblin[14] for American oils, and by Mendelejeff[15] for Russian.

Cryoscopic "Molecular Weight."—The average "molecular weights" of the 50° cuts between 150° and 300° were determined by the cryoscopic method, using benzol as a solvent. No measurements were made on fractions boiling below 150° because of the possible presence of benzol in these distillates.

The concentration of solute was kept practically constant and to eliminate possible variations due to association so as to make all determinations comparable. The values of solute were between 0.12 to 0.15 of a gm., whereas the solvent weighed from 13 to 18 gms. The temperature readings were made with a Reichsanstalt certified Beckmann thermometer. The solvent used was Kahlbaum's thiophen-free, recrystallized benzol. The benzol was further purified by the method advocated by Richards[16] and Shipley for freezing point in thermometry.

Every experimental precaution was taken to eliminate errors due to impurity of solvent, weighing vessels and thermometer. The average "molecular weights" as determined are given in Table LXXXII.

It appeared from these experiments that "molecular weights" did not exhibit an agreement with the values for specific gravity and refractive index. Neither was there any agreement between "molecular weights" and surface tension or capillary constant.

It also appeared that "molecular weights" were lower than would be indicated from calculations concerning hydrocarbons boiling between the given temperature limits. This discrepancy is probably due to the fact that the actual average boiling temperature of a cut obtained on distilling a crude oil is lower than the average indicated by the given limits.

Ultimate Analysis.—Eight samples of distillates of b.p. 200 to 250° were analyzed for the carbon and hydrogen content. The results appear in Table LXXXIII and indicate for a number of American

TABLE LXXXIII

ULTIMATE ANALYSES OF CERTAIN 200 TO 250° B. P. FRACTIONS

Sample No.	269	1281	816	Kern	S. M.	Mex.	R. M.	R. R.
Per cent hydrogen......	13.62	13.90	14.57	13.40	13.07	13.34	13.42	13.31
Per cent carbon.........	86.36	85.37	84.99	86.27	85.42	85.00	86.34	84.49

[14] *Ber.*, 16, 1873.
[15] Rakusin, *Untersuch d. Erdols.*
[16] *J. Am. Chem. Soc.*, 36 (1914), 1825.

TABLE LXXXIV

PHYSICAL CONSTANTS OF DISTILLATION CUTS IN ORDER OF SPECIFIC GRAVITIES

FRACTION B. P. UP TO 100° C.

Sample	815	1336	765	764	816	269	1339	Heald	1280	1281	273	S. M.	R. R.	R. M.	587	591	Mex.
Sp. gr.	0.670	0.680	0.682	0.686	0.686	0.688	0.689	0.690	0.705	...	0.706	0.706	...	0.733	...	...	...
Ref. ind.	1.375	1.385	1.385	1.385	1.386	1.386	1.387	1.388	1.398	...	1.390	1.392	1.401	1.403	1.423	...	...
Sur. ten.	19.11	19.85	18.87	18.81	19.53	19.54	18.92	19.71	19.99	...	18.92	20.78	...	21.19	...	...	...
Cap. const.	5.86	6.00	5.69	5.64	5.84	5.84	5.64	5.86	5.82	...	5.50	6.04	...	5.93	...	...	...

FRACTION B. P. BETWEEN 100° AND 150°

Sample	764	815	816	1280	765	1336	1339	Heald	269	1281	Mex.	273	S. M.	R. R.	R. M.	Kern	591
Sp. gr.	0.736	0.737	0.740	0.746	0.748	0.749	0.752	0.754	0.756	0.757	0.759	0.762	0.762	0.767	0.769	...	...
Ref. ind.	1.407	1.408	1.410	1.141	1.416	1.416	1.416	1.418	1.418	1.419	1.419	1.419	1.420	1.421	1.423	1.434	...
Sur. ten.	21.95	21.67	20.98	22.05	21.87	22.09	21.53	22.34	22.12	22.69	...	22.33	22.47	22.75	22.80	...	...
Cap. const.	5.84	6.03	5.81	6.06	6.13	6.05	5.88	6.07	6.00	6.15	...	6.01	6.06	6.08	6.08	...	...

FRACTION B. P. BETWEEN 150° AND 200°

Sample	764	815	816	765	1280	1336	1281	1339	Heald	269	Mex.	R. R.	273	R. M.	S. M.	Kern	591
Sp. gr.	0.766	0.767	0.771	0.780	0.781	0.783	0.785	0.785	0.791	0.792	0.798	0.804	0.805	0.806	0.806	0.820	0.826
Ref. ind.	1.425	1.426	1.427	1.430	1.431	1.432	1.434	1.434	1.435	1.436	1.439	1.439	1.440	1.441	1.444	1.445	1.448
Sur. ten.	23.29	23.75	22.64	24.00	24.25	24.07	24.35	22.91	23.98	22.70	24.62	24.85	24.55	24.93	25.31	25.25	25.36
Cap. const.	6.23	6.35	6.02	6.46	6.32	6.31	6.36	5.99	6.21	5.87	6.33	6.34	6.25	6.34	6.44	6.30	6.29
Mol. wt.	138	140	130	122	132	131	138	131	128	133	143	128	126	119	126	131	143

FRACTION B. P. BETWEEN 200° AND 250°

Sample	764	815	816	765	1336	1339	1280	1281	Heald	269	R. R.	R. M.	Mex.	S. M.	273	Kern	591
Sp. gr.	0.789	0.792	0.793	0.799	0.809	0.812	0.814	0.815	0.818	0.825	0.836	0.836	0.843	0.846	0.851	0.858	0.860
Ref. ind.	1.437	1.438	1.439	1.443	1.448	1.448	1.449	1.450	1.451	1.455	1.457	1.457	1.464	1.465	1.465	1.465	1.465
Sur. ten.	25.04	25.42	23.67	25.29	25.61	23.91	26.13	26.12	24.00	23.47	26.50	26.71	26.36	26.28	26.43	28.62	27.22
Cap. const.	6.51	6.58	6.12	6.61	6.49	6.03	6.57	6.56	6.26	5.82	6.49	6.55	6.39	6.36	6.36	6.83	6.48
Mol. wt.	165	167	149	159	166	154	158	170	160	167	146	141	178	140	152	151	179

FRACTION B. P. BETWEEN 250° AND 300°

Sample	764	816	815	765	1336	1339	1280	1281	Heald	269	R. R.	R. M.	Mex.	S. M.	Kern	591	273
Sp. gr.	0.812	0.813	0.815	0.818	0.831	0.836	0.839	0.813	0.839	0.855	0.861	0.861	0.871	0.878	0.887	0.890	0.891
Ref. ind.	1.449	1.449	1.449	1.452	1.459	1.461	1.464	1.464	1.465	1.472	1.472	1.474	1.481	1.483	1.484	1.484	1.493
Sur. ten.	26.47	24.48	26.80	26.84	27.02	24.45	27.48	27.37	26.01	23.81	27.15	28.01	27.26	28.04	29.51	28.03	28.18
Cap. const.	6.68	6.16	6.73	6.79	6.66	5.99	6.71	6.68	6.34	5.71	6.46	6.67	6.41	6.54	6.81	6.45	6.47
Mol. wt.	203	181	206	184	214	191	196	212	193	192	171	181	198	180	182	194	173

oils, practically pure hydrocarbons with small amounts of oxygen, nitrogen or sulfur compounds, whereas one Russian and the Mexican oil show a relatively high per cent of oxygen, nitrogen or sulfur compounds, which might bear out the statement as to small amounts of certain extraneous substances greatly changing the surface tensions of pure hydrocarbons.

The relations existing among the various sets of constants are shown by two comparison tables. Table LXXXIV represents a cut boiling up to 100°, from 100 to 150°, from 150 to 200°, from 200 to 250°, and from 250 to 300°. Table LXXXV represents data on combined cuts up to 150°, generally classed by petroleum technologists as "naphtha," and combined cuts from 150 to 300°, generally classed as "kerosene."

Comparisons are best made by the use of the graphs of Figure 165 plotted from the values for the last three series in Table LXXXIV. These are representative of the results of all the other tables and were selected because they include the most comprehensive lists of constants.

The graphs are plotted using as abscissas equidistant points, each representing a different oil. The oils are arranged in such order as to give an ascending curve for specific gravities. An inspection of the graphs shows that the only constant bearing any clear-cut relation to specific gravity is refractive index.

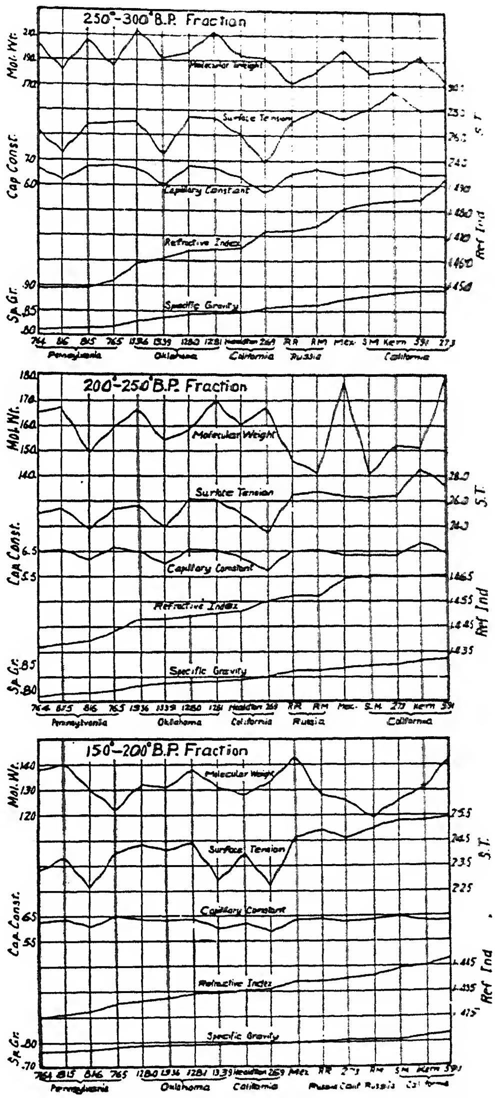

FIG. 165.—Relationships Between Physical Constants of Petroleum Distillates.

The curve for surface tension is decidedly irregular but shows a tendency to slope upwards. This indicates that among petroleum hydrocarbons surface tension varies in the same direction as specific gravity. This constant is, however, so strongly affected by small variations in chemical composition that it is at present of little value as a means of identification. It is hoped, however, that later these irregularities may be understood well enough to furnish scientific as well as useful industrial information.

TABLE LXXXV

PHYSICAL CONSTANTS OF "NAPHTHA" AND "KEROSENE" CUTS OF OILS STUDIED

Naphtha—B. P. up to 150° C.					*Kerosene*—B. P. 150° to 300°				
Sample No.	Sp. gr.	Refr. index	Surf. tens.	Cap. const.	Sample No.	Sp. gr.	Refr. index	Surf. tens.	Cap. const.
815	0.706	1.392	19.96	5.82	815	0.789	1.437	24.73	6.44
764	0.716	1.398	20.54	5.88	764	0.790	1.438	25.07	6.50
816	0.722	1.400	20.02	5.69	816	0.792	1.439	23.96	6.20
1336	0.726	1.402	20.52	5.79	765	0.795	1.440	24.66	6.43
765	0.731	1.405	19.34	5.57	1336	0.808	1.445	25.59	6.49
269	0.733	1.406	21.12	5.92	1281	0.811	1.448	26.80	6.66
Heald	0.734	1.406	20.38	5.69	1339	0.814	1.449	23.91	6.02
1339	0.736	1.407	19.41	5.41	1280	0.815	1.451	25.04	6.30
1280	0.741	1.410	20.28	5.61	269	0.820	1.452	23.18	5.77
S. M.	0.744	1.410	21.34	5.87	Heald	0.824	1.454	25.27	6.28
273	0.750	1.412	20.74	5.67	R. R.	0.836	1.458	26.34	6.45
R. M.	0.765	1.418	22.37	5.99	R. M.	0.841	1.459	26.57	6.46
					273	0.842	1.463	25.50	6.20
					S. M.	0.849	1.466	26.40	6.37
					Mex.	0.861	1.475	26.96	6.40
					Kern	0.878	1.476	27.79	6.48
					591	0.878	1.476	26.87	6.26

Capillary constant curves show the same irregularities as those of surface tension but lack the slope upward. This is to be expected when the method of derivation of this constant is considered.

In considering the "molecular-weight" graph, it appears that the agreement of this constant with specific gravity, though theoretically to be expected, is conspicuous by its absence. No satisfactory explanation appears except that there is some inherent error in the method here employed for the determination of molecular weights. Present experience indicates that the measurement of this constant by the cryoscopic method with benzol as a solvent is of doubtful value in the identification of petroleum distillates. The experimental values are recorded with a full knowledge of their being "so-called Molecular Weights."

CONCLUSIONS.

I—The present series of experiments has tended to justify the methods of identification (distillation, specific gravity and refractive index) usually employed in petroleum testing laboratories.

II—Volatility and specific gravity are the two most important constants and a knowledge of these two is generally sufficient for the identification of an oil.

III—Refractive indices vary in the same direction as specific gravities. When only small quantities of distillates are available, determinations of the former are more convenient than measurements of specific gravities.

IV—Surface tension is a constant not yet of value. This is on account of our lack of knowledge regarding variations caused by the probable presence of small quantities of certain substances in crude petroleums. Surface tensions in general seem to increase with specific gravity when relations among petroleum hydrocarbons are considered.

V—Cryoscopic "molecular weights," as measured by the cryoscopic method with benzene as a solvent, are of questionable value in the study of mixtures of petroleum products.

Coefficient of Expansion of Petroleum Oils.

The density and coefficient of expansion of all American petroleum products of densities ranging from 0.620 to 0.950 have been determined by the U. S. Bureau of Standards, for temperatures between 30 to 120° F. In addition heavy fuel and lubricating oils have been examined at temperatures up to 210° F. This is the most authoritative work on this subject. The methods used and results obtained are given in detail in Technologic Paper No. 77 of the U. S. Bureau of Standards, and are the basis of "United States Standard Tables for Petroleum Oils" published as Circular 57 of the U. S. Bureau of Standards.

The investigation showed that within the limits of accuracy of ordinary measurements the coefficient of expansion, or the change of specific gravity with temperature, are the same for all oils of the same specific gravity.

The expansion of any sample is given by the equations:

$D_t = D_T + \alpha (t-T) + \beta (t-T)^2$ in which

D_t = density at any temperature "t"

D_T = density at the standard temperature "T."

α and β are constant coefficients.

The results are given herewith in tabulated form.

TABLE LXXXVI

Densities of Refined Distillates and Oils at Several Temperatures, and Values of the Coefficients α and β.

Locality produced	Nature of oil	Density (g/ml) at—							$\alpha \times 10^5$	$\beta \times 10^7$
		0°	10°	20°	25°	30°	40°	50°		
	Pentane	0.6388	....	....	0.6131	....	....	....	103	....
	....do	.6410	....	....	.6164	....	....	....	98	....
	....do	.6564	....	....	.6321	....	....	....	97	....
	....do	.6562	....	....	.6324	....	....	....	95	....
	Naphtha	.7002	0.6914	0.6825	.6781	0.6736	0.6647	0.6558	89	—1
	Gasoline	.7193	.7107	.7020	.6975	.6933	.6845	.6757	87	—2
	Naphtha	.7237	.7150	.7062	.7019	.6975	.6887	.6798	88	—2
Texas	Gasoline	.7506	.7422	.7339	.7296	.7256	.7172	.7087	84	—1
Pennsylvania	....do	.7515	.7433	.7351	.7310	.7270	.7188	.7105	82	—1
California	Gasoline (treated)	.7532	.7447	.7362	.7319	.7277	.7190	.7104	86	—3
Do	Benzine (treated)	.7641	.7556	.7473	.7431	.7389	.7305	.7220	84	—1
Indiana	Naphtha	.7657	.7575	.7493	.7453	.7411	.7328	.7244	82	—2
California	Engine distillate	.7879	.7799	.7719	.7679	.7639	.7559	.7478	80	—1
Oklahoma	Gasoline	.7949	.7874	.7798	.7760	.7722	.7645	.7568	76	—2
Pennsylvania	Kerosene	.7981	.7908	.7835	.7799	.7762	.7689	.7615	73	—1
Do	....do	.7990	.7918	.7845	.7809	.7772	.7700	.7627	73	0
Do	....do	.7994	.7921	.7848	.7812	.7775	.7702	.7629	73	0
Louisiana	Lighthouse oil	.8017	.7944	.7872	.7835	.7799	.7726	.7650	73	—2
Pennsylvania	Kerosene	.8040	.7968	.7896	.7860	.7824	.7753	.7681	72	0
Do	....do	.8054	.7982	.7910	.7874	.7838	.7766	.7694	72	0
Ohio	....do	.8096	.8023	.7949	.7913	.7876	.7802	.7729	73	—1
Indiana	Refined	.8128	.8054	.7979	.7942	.7905	.7830	.7756	74	—1
Oklahoma	Kerosene	.8136	.8062	.7989	.7953	.7916	.7842	.7769	73	0
Mid-continent	....do	.8177	.8104	.8030	.7994	.7957	.7883	.7809	74	0
California	....do	.8249	.8175	.8101	.8064	.8027	.7953	.7878	74	0
Do	....do	.8301	.8228	.8155	.8119	.8082	.8009	.7935	73	0
	Burning oil (high F. T.)	.8389	....	....	.8220	....	....	.8053	67	....
Louisiana	Mineral Seal	.8390	.8322	.8254	.8221	.8187	.8119	.8052	68	0
Pennsylvania	Refined	.8573	.8507	.8440	.8407	.8374	.8308	.8243	66	+1

Indiana	....do	.8614	.8546	.8478	.8444	.8410	.8343	.8275	68	+1
	Neutral	.8646	....	....	.8481	....	....	.8317	66	....
	....do	.8714	....	....	.8551	....	....	.8388	65	....
California	Stove oil (treated)	.8763	.8692	.8620	.8585	.8550	.8479	.8408	71	+1
Pennsylvania	Refined	....	.8703	.8638	.8606	.8574	.8510	.8447	64	+3
Do	Dynamo oil	.8800	.8736	.8672	.8639	.8607	.8542	.8478	64	0
Do	Refined	.8802	.8735	.8671	.8639	.8607	.8544	.8481	64	+3
Louisiana	....do	.8832	....	....	.8661	....	....	.8498	67	....
	Neutral	.8834	....	....	.8672	....	....	.8512	65	....
Pennsylvania	Refined	.8841	.8782	.8718	.8688	.8657	.8594	.8531	62	−3
	Marine engine	.8938	....	....	.8766	....	....	.8609	66	....
	Gas engine	.8974	....	....	.8810	....	....	.8651	65	....
Louisiana	Refined	.9007	....	....	.8838	....	....	.8678	66	....
	Cylinder oil	.9108	....	....	.8910	....	....	.8730	[a] 76	....
	Paraffin oil	.9118	....	....	.8947	....	....	.8786	66	....
Indiana	Refined	.9111	.9045	.8980	.8948	.8915	.8850	.8786	65	+1
	Engine oil	.9124	.9053	.8988	.8956	.8924	.8859	.8794	[a] 66	+14
	Cylinder oil	.9153	....	....	.8971	....	....	.8803	70	....
	Paraffin oil	.9205	....	....	.9036	....	....	.8876	66	....
	Cylinder oil	.9285	....	....	.9086	....	....	.8912	[a] 75	....
Texas	Refined	.9385	.9319	.9252	.9219	.9186	.9110	.9054	66	−1
Indiana	....do	.9421	....	....	.9221	....	....	.9052	[a] 74	....
	Gas engine oil	.9470	....	....	.9306	....	....	.9145	65	....
Texas	Refined	.9497	....	....	.9333	....	....	.9173	65	....
Do	....do	.9551	....	....	.9389	....	....	.9230	64	....

[a] These samples probably contained solid particles at the low temperatures.

(TABLE LXXXVI—*Continued*)

CRUDE OILS

Locality produced	D_0 g/ml	α^1 0°–25°	D_{25} g/ml	α^1 25°–50°	D_{50} g/ml
Pennsylvania	0.8253	0.00074	0.8067	0.00070	0.7892
Louisiana	.8309	.00076	.8118	.00071	.7940
Texas	.8425	.00074	.8241	.00072	.8061
Pennsylvania	.8432	.00072	.8251	.00069	.8078
Louisiana	.8526	.00065	.8363	.00065	.8200
Ohio	.8648	.00076	.8459	.00068	.8288
Mid-continent	.8726	.00067	.8553	......	.....
Oklahoma	.8815	.00074	.8629	.00068	.8460
California	.9082	.00070	.8908	.00070	.8734
Do.	.9162	.00067	.8995	.00067	.8828
Louisiana	.9193	.00069	.9021	.00068	.8850
Texas	.9232	.00068	.9062	.00066	.8897
California	.9361	.00071	.9183	.00068	.9012
			D_{30} g/ml	α^1 30°–40°	D_{40} g/ml
Texas	.....	......	.9180	.00071	.9109
Do.	.....	......	.9194	.00066	.9128
Do.	.....	......	.9296	.00067	.9229
Do.	.....	......	.9396	.00068	.9328
California	.....	......	.9564	.00066	.9498

TABLE LXXXVI—(*Continued*)

FUEL OILS AND HEAVY LUBRICATING OILS

Nature of oil	D_{25} g/ml	α^1 25°–50°	D_{50} g/ml	α^1 50°–75°	D_{75} g/ml	α^1 75°–95°	D_{95} g/ml
Autocylinder	0.8620	0.00063	0.8462	0.00064	0.8303	0.00063	0.8177
Fuel	.8641	.00068	.8472	.00067	.8304	.00068	[a] .8168
Autocylinder	.8651	.00064	.8492	.00063	.8335	.00063	.8209
Fuel	.8713	.00067	.8546	.00066	.8380	.00068	[a] .8144
Gas engine	.8809	.00063	.8652	.00062	.8496	.00062	.8373
Locomotive	.9003	.00068	.8833	.00062	.8678	.00062	.8555
Noncondensing cylinder	.9010	.00069	.8838	.00061	.8686	.00062	.8563
Locomotive	.9140	.00068	.8971	.00063	.8814	.00064	.8687
Marine engine	.9171	.00065	.9009	.00064	.8848	.00064	.8720
Gas engine	.9202	.00064	.9043	.00064	.8884	.00064	.8757
Do.	.9204	.00064	.9044	.00064	.8885	.00064	.8758
Stationary engine	.9285	.00064	.9126	.00063	.8968	.00063	.8842
Marine engine	.9386	.00064	.9225	.00064	.9065	.00064	.8936
Fuel	.9526	.00065	.9363	.00066	.9199	.00066	[a] .9066
Do.	.9537	.00065	.9374	.00065	.9212	.00065	.9082

[a] Calculated from the density at 85° C. α^1 is the change of density per degree centigrade.

TABLE LXXXVII

AVERAGE VALUES OF THE COEFFICIENTS α AND β FOR PETROLEUM PRODUCTS OF DIFFERENT DENSITIES

D 25° C.	α	β	D 25° C.	α	β
0.62	−0.00099	−0.0000004	0.79	−0.00073	0.0000000
0.63	.00097	.0000003	0.80	.00072	.0000000
0.64	.00095	.0000003	0.81	.00071	.0000000
0.65	.00094	.0000003	0.82	.00070	.0000000
0.66	.00092	.0000003	0.83	.00070	.0000000
0.67	.00091	.0000003	0.84	.00069	.0000000
0.68	.00090	.0000002	0.85	.00068	+.0000001
0.69	.00088	.0000002	0.86	.00068	.0000001
0.70	.00087	.0000002	0.87	.00068	.0000001
0.71	.00086	.0000002	0.88	.00067	.0000001
0.72	.00084	.0000002	0.89	.00067	.0000002
0.73	.00083	.0000001	0.90	.00067	.0000002
0.74	.00081	.0000001	0.91	.00066	.0000002
0.75	.00080	.0000001	0.92	.00066	.0000002
0.76	.00078	.0000001	0.93	.00066	.0000002
0.77	.00077	.0000001	0.94	.00066	.0000002
0.78	.00075	.0000000	0.95	.00066	.0000003

TABLE LXXXVIII

TEMPERATURE CORRECTIONS OF SPECIFIC GRAVITIES OF AMERICAN PETROLEUM OILS

(Standard to 60°/60° F.)

Observed Temp. F.	Observed Specific Gravity 0.650	0.700	0.750	0.800	0.850	0.900	0.950
	Subtract from Observed Specific Gravity						
30	0.016	0.015	0.014	0.012	0.011	0.011	0.011
32	.015	.014	.013	.012	.011	.010	.010
34	.014	.013	.012	.011	.010	.010	.010
36	.013	.012	.011	.010	.009	.009	.009
38	.012	.011	.010	.009	.008	.008	.008
40	.0105	.0095	.0090	.0080	.0075	.0070	.0070
42	.0095	.0085	.0080	.0070	.0065	.0065	.0065
44	.0085	.0075	.0070	.0065	.0060	.0060	.0055
46	.0075	.0065	.0060	.0055	.0050	.0050	.0050
48	.0065	.0060	.0055	.0050	.0045	.0045	.0040
50	.0050	.0050	.0045	.0040	.0035	.0035	.0035
52	.0040	.0040	.0035	.0030	.0030	.0030	.0030
54	.0030	.0030	.0025	.0025	.0020	.0020	.0020
56	.0020	.0020	.0020	.0015	.0015	.0015	.0015
58	.0010	.0010	.0010	.0005	.0005	.0005	.0005
	Add to Observed Specific Gravity						
60	.0000	.0000	.0000	.0000	.0000	.0000	.0000
62	.0010	.0010	.0010	.0005	.0005	.0005	....
64	.0020	.0020	.0015	.0015	.0015	.0015	....
66	.0030	.0030	.0025	.0025	.0020	.0020	....
68	.0040	.0040	.0035	.0030	.0030	.0030	....
70	.0050	.0050	.0045	.0040	.0040	.0035	....
72	.0060	.0055	.0050	.0045	.0045	.0040	....
74	.0070	.0065	.0060	.0055	.0050	.0050	....
76	.0080	.0075	.0070	.0065	.0060	.0055	....
78	.0090	.0085	.0080	.0070	.0065	.0065	....
80	.010	.009	.008	.008	.007	.007	....
82	.011	.010	.009	.008	.008	.007	....
84	.012	.011	.010	.009	.009	.008	....
86	.013	.012	.011	.010	.009	.009	....
88	.014	.013	.012	.011	.010	.010	....
90	.015	.014	.013	.012	.011	.010	....
92	.016	.015	.013	.012	.011	.011	....
94	.017	.016	.014	.013	.012	.012	....
96	.018	.016	.015	.014	.013	.013	....
98	.019	.017	.016	.015	.014	.013	....
100	.020	.018	.017	.015	.014	.014	....
102	.021	.019	.018	.016	.015	.015	....
104	.022	.020	.018	.017	.016	.015	....
106	.023	.021	.019	.017	.016	.016	....
108	.024	.022	.020	.018	.017	.017	....
110	.025	.023	.021	.019	.018	.017	....
112	.026	.024	.022	.020	.019	.018	....
114	.027	.025	.022	.020	.019	.019	....
116	.028	.026	.023	.021	.020	.019	....
118	.029	.026	.024	.022	.021	.020	....
120	.030	.027	.025	.023	.022	.021	....

TABLE LXXXIX

TEMPERATURE CORRECTIONS OF A. P. I. GRAVITIES OR BAUMÉ GRAVITIES OF AMERICAN PETROLEUM OILS

(Standard at 60° F.)

Observed Tempera-ture F.	Observed Degrees A. P. I. or Baumé							
	20.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0
	Add to Observed Degrees A. P. I. or Baumé							
30	1.7	2.0	2.4	3.0	3.7	4.3	5.0	5.7
32	1.6	1.9	2.3	2.8	3.4	4.0	4.7	5.3
34	1.5	1.8	2.1	2.6	3.1	3.7	4.3	4.9
36	1.4	1.6	2.0	2.4	2.9	3.4	4.0	4.6
38	1.3	1.5	1.8	2.2	2.6	3.1	3.6	4.2
40	1.2	1.4	1.6	2.0	2.4	2.8	3.2	3.8
42	1.1	1.2	1.5	1.8	2.2	2.5	2.9	3.4
44	.9	1.1	1.3	1.6	2.0	2.2	2.6	3.0
46	.8	.9	1.1	1.4	1.7	1.9	2.3	2.7
48	.7	.8	.9	1.2	1.4	1.6	2.0	2.3
50	.6	.7	.8	1.0	1.2	1.4	1.6	1.9
52	.5	.6	.7	.8	1.0	1.1	1.3	1.5
54	.3	.4	.5	.6	.8	.9	1.0	1.1
56	.2	.3	.3	.4	.5	.6	.6	.7
58	.1	.1	.1	.2	.3	.3	.3	.4
	Subtract from Degrees A. P. I. or Baumé							
60	.0	.0	.0	.0	.0	.0	.0	.0
62	.1	.1	.1	.2	.2	.3	.3	.4
64	.2	.3	.3	.4	.4	.6	.6	.7
66	.3	.4	.5	.6	.7	.8	.9	1.0
68	.5	.6	.6	.7	.9	1.1	1.3	1.4
70	.6	.7	.8	.9	1.1	1.4	1.6	1.7
72	.7	.8	.9	1.1	1.3	1.6	1.9	2.1
74	.8	.9	1.1	1.3	1.6	1.8	2.2	2.5
76	.9	1.1	1.3	1.5	1.8	2.1	2.5	2.8
78	1.0	1.2	1.4	1.7	2.0	2.4	2.8	3.1
80	1.1	1.3	1.5	1.8	2.2	2.6	3.1	3.5
82	1.2	1.4	1.7	2.0	2.5	2.9	3.4	3.9
84	1.3	1.5	1.8	2.2	2.7	3.2	3.7	4.3
86	1.4	1.7	2.0	2.4	2.9	3.4	4.0	4.6
88	1.6	1.8	2.1	2.6	3.1	3.7	4.2	4.9
90	1.7	2.0	2.3	2.7	3.3	3.9	4.5	5.2
92	1.8	2.1	2.4	2.9	3.5	4.2	4.8	5.6
94	1.9	2.2	2.6	3.1	3.8	4.4	5.1	5.9
96	2.0	2.3	2.7	3.3	4.0	4.6	5.4	6.3
98	2.1	2.4	2.9	3.4	4.2	4.9	5.7	6.6
100	2.2	2.6	3.0	3.6	4.4	5.1	6.0	6.9
102	2.3	2.7	3.2	3.8	4.6	5.4	6.3	7.2
104	2.4	2.9	3.3	4.0	4.8	5.7	6.6	7.5
106	2.5	3.0	3.5	4.2	5.0	5.9	6.9	7.9
108	2.7	3.1	3.6	4.3	5.2	6.2	7.2	8.2
110	2.8	3.2	3.7	4.4	5.4	6.4	7.5	8.5
112	2.9	3.3	3.9	4.6	5.6	6.7	7.7	8.8
114	3.0	3.4	4.0	4.7	5.8	6.9	7.9	9.1
116	3.1	3.6	4.1	4.9	6.0	7.1	8.2	9.4
118	3.2	3.7	4.3	5.1	6.2	7.3	8.5	9.8
120	3.3	3.8	4.4	5.3	6.4	7.5	8.8	10.1

Method of Correcting Volume of Oil for Temperature Variations.

The task of making the hundreds of corrections of volume of oils at some temperature to the corresponding volume at the standard temperature 60° F. involves no small amount of labor and time. Dr. T. G. Delbridge of the Atlantic Refining Company has published[17] tables used by this corporation. Table XC, including parts A, B, C, D, E, and F, given below is that of Dr. Delbridge. The method of using it is as follows: (1) Select the proper table according to the nature of the material. (2) Find in this table the multiplier corresponding to the temperature of measurement. (3) Multiply gage gallon at temperature of measurement by this multiplier; product is gallons at 60° F.

EXAMPLES. 10239 gallons of motor gasoline at 72° F. is equivalent to 10165.3 gallons at 60° F. Part C applies to motor gasoline; multiplier from Part C for 72° F. is 0.9928; 10239 × 0.9928 = 10165.2792.

8137 gallons of Safety Solvent at 80° F. is equivalent to 8056.4 gallons at 60 degrees. Part D applies to Safety Solvent. Multiplier for Part D for 80° F. is 0.9901; 8137 × 0.9901 = 8056.4437.

These tables are based on coefficients of expansion taken from Bureau of Standards Technologic Paper No. 77 and cover the following ranges:

	Coeff. of Expansion	Gravity Range
Part A	0.0008	79.0 and lighter
B	0.0007	78.9–65.0
C	0.0006	64.9–51.0
D	0.0005	50.9–35.0
E	0.0004	heavier than 35.0
F	0.00038	Pitches

The method of calculating the individual multipliers for the tables is as follows:

$$\text{Multiplier} = \frac{1}{1 + [\text{coeff. of exp.} \times (\text{temp.} - 60^\circ\ \text{F.})]}$$

Thus at 40° F. with coeff. 0.0006 the proper multiplier is:

$$\frac{1}{1 + [.0006 \times (40\text{-}60)]} = \frac{1}{1 - .0120} = 1.0121$$

[17] *Nat. Pet. News*, June 28, 1922, 41.

TABLE XC

DELBRIDGE'S VOLUME CORRECTION MULTIPLIERS

	...of ...sed ...an-		
	Mu plie	Degr	Multi-plier
1	1.0495	46	1.0113
2	1.0487	47	1.0105
3	1.0478	48	1.0097
4	1.0469	49	1.0089
5	1.0460	50	1.0081
6	1.0452	51	1.0073
7	1.0443	52	1.0064
8	1.0434	53	1.0056
9	1.0425	54	1.0048
10	1.0417	55	1.0040
11	1.0408	56	1.0032
12	1.0399	57	1.0024
13	1.0391	58	1.0016
14	1.0382	59	1.0008
15	1.0373	60	1.0000
16	1.0365	61	.9992
17	1.0356	62	.9984
18	1.0348	63	.9976
19	1.0339	64	.9968
20	1.0331	65	.9960
21	1.0322	66	.9952
22	1.0314	67	.9944
23	1.0305	68	.9936
24	1.0297	69	.9929
25	1.0288	70	.9921
26	1.0280	71	.9913
27	1.0271	72	.9905
28	1.0263	73	.9897
29	1.0254	74	.9889
30	1.0246	75	.9881
31	1.0238	76	.9873
32	1.0229	77	.9866
33	1.0221	78	.9858

PART B. Applying to gravities of 78.9-65.0. Based on co-efficient of expansion of 0.0007.			
Degree	Multi-plier	Degree	Multi-plier
1	1.0431	51	1.0064
2	1.0423	52	1.0057
3	1.0416	53	1.0050
4	1.0408	54	1.0043
5	1.0400	55	1.0036
6	1.0393	56	1.0029
7	1.0385	57	1.0022
8	1.0378	58	1.0015
9	1.0370	59	1.0008
10	1.0362	60	1.0000
11	1.0355	61	.9993
12	1.0348	62	.9986
13	1.0340	63	.9979
14	1.0333	64	.9972
15	1.0325	65	.9965
16	1.0318	66	.9958
17	1.0310	67	.9951
18	1.0303	68	.9944
19	1.0295	69	.9937
20	1.0288	70	.9930
21	1.0281	71	.9924
22	1.0273	72	.9917
23	1.0266	73	.9910
24	1.0259	74	.9903
25	1.0251	75	.9896
26	1.0244	76	.9889
27	1.0236	77	.9882
28	1.0229	78	.9876
29	1.0222	79	.9869
30	1.0214	80	.9862
31	1.0207	81	.9855
32	1.0200	82	.9848
33	1.0193	83	.9842

PART C. Applying to gravities 64.9-51.0. Based on co-efficient of expansion 0.0006.			
Degree	Multi-plier	Degree	Multi-plier
1	1.0367	61	.9994
2	1.0361	62	.9988
3	1.0354	63	.9982
4	1.0348	64	.9976
5	1.0341	65	.9970
6	1.0335	66	.9964
7	1.0328	67	.9958
8	1.0322	68	.9952
9	1.0316	69	.9946
10	1.0309	70	.9940
11	1.0303	71	.9934
12	1.0297	72	.9928
13	1.0290	73	.9923
14	1.0284	74	.9917
15	1.0277	75	.9911
16	1.0271	76	.9905
17	1.0265	77	.9899
18	1.0259	78	.9893
19	1.0252	79	.9887
20	1.0246	80	.9881
21	1.0240	81	.9876
22	1.0233	82	.9870
23	1.0227	83	.9864
24	1.0221	84	.9858
25	1.0215	85	.9852
26	1.0208	86	.9846
27	1.0202	87	.9841
28	1.0196	88	.9835
29	1.0190	89	.9829
30	1.0183	90	.9823
31	1.0177	91	.9817
32	1.0171	92	.9812
33	1.0165	93	.9806

PART D. Applying to gravities 50.9-35.0. Based on co-efficient of expansion 0.0005.			
Degree	Multi-plier	Degree	Multi-plier
1	1.0304	61	.9995
2	1.0299	62	.9990
3	1.0293	63	.9985
4	1.0288	64	.9980
5	1.0283	65	.9975
6	1.0277	66	.9970
7	1.0272	67	.9965
8	1.0267	68	.9960
9	1.0262	69	.9955
10	1.0256	70	.9950
11	1.0251	71	.9945
12	1.0246	72	.9940
13	1.0241	73	.9935
14	1.0235	74	.9930
15	1.0230	75	.9926
16	1.0225	76	.9921
17	1.0220	77	.9916
18	1.0215	78	.9911
19	1.0209	79	.9906
20	1.0204	80	.9901
21	1.0199	81	.9896
22	1.0194	82	.9891
23	1.0188	83	.9886
24	1.0183	84	.9881
25	1.0178	85	.9877
26	1.0173	86	.9872
27	1.0168	87	.9867
28	1.0163	88	.9863
29	1.0157	89	.9857
30	1.0152	90	.9852
31	1.0147	91	.9847
32	1.0142	92	.9843
33	1.0137	93	.9838

PART E. Applying to gravities heavier than 35.0. Based on co-efficient of expansion 0.0004.			
Degree	Multi-plier	Degree	Multi-plier
1	1.0242	151	.9649
2	1.0238	152	.9645
3	1.0233	153	.9641
4	1.0229	154	.9638
5	1.0225	155	.9634
6	1.0221	156	.9630
7	1.0217	157	.9626
8	1.0212	158	.9623
9	1.0208	159	.9619
10	1.0204	160	.9615
11	1.0200	161	.9612
12	1.0196	162	.9608
13	1.0192	163	.9604
14	1.0187	164	.9600
15	1.0183	165	.9597
16	1.0179	166	.9593
17	1.0175	167	.9590
18	1.0171	168	.9586
19	1.0167	169	.9582
20	1.0163	170	.9579
21	1.0158	171	.9575
22	1.0154	172	.9571
23	1.0150	173	.9568
24	1.0146	174	.9564
25	1.0142	175	.9560
26	1.0138	176	.9557
27	1.0134	177	.9553
28	1.0130	178	.9549
29	1.0126	179	.9546
30	1.0121	180	.9542
31	1.0117	181	.9538
32	1.0113	182	.9535
33	1.0109	183	.9531

PART F. Applying to Pitches. Based on co-efficient of expansion 0.00038.			
Degree	Multi-plier	Degree	Multi-plier
40	1.0077	300	.9164
45	1.0057	305	.9148
50	1.0038	310	.9132
55	1.0019	315	.9117
60	1.0000	320	.9101
65	.9981	325	.9085
70	.9962	330	.9069
75	.9943	335	.9054
80	.9925	340	.9038
85	.9906	345	.9023
90	.9887	350	.9007
95	.9869	355	.8992
100	.9850	360	.8977
105	.9832	365	.8961
110	.9814	370	.8946
115	.9795	375	.8931
120	.9777	380	.8916
125	.9759	385	.8901
130	.9741	390	.8886
135	.9723	395	.8871
140	.9705	400	.8856
145	.9687	405	.8841
150	.9669	410	.8826
155	.9652	415	.8811
160	.9634	420	.8797
165	.9616	425	.8782
170	.9599	430	.8767
175	.9581	435	.8753
180	.9564	440	.8738
185	.9547	445	.8724
190	.9529	450	.8709
195	.9512	455	.8695
200	.9495	460	.8681

34	1.0212	79	.9850	34	1.0185	84	.9835	34	1.0158	94	.9800	34	1.0132	94	.9833	34	1.0105	184	.9527	205	.9478	465	.8666
35	1.0204	80	.9843	35	1.0178	85	.9828	35	1.0152	95	.9794	35	1.0127	95	.9828	35	1.0101	185	.9524	210	.9461	470	.8652
36	1.0196	81	.9835	36	1.0172	86	.9821	36	1.0146	96	.9789	36	1.0121	96	.9823	36	1.0097	186	.9520	215	.9444	475	.8638
37	1.0187	82	.9827	37	1.0165	87	.9815	37	1.0140	97	.9783	37	1.0116	97	.9818	37	1.0093	187	.9517	220	.9427	480	.8624
38	1.0179	83	.9819	38	1.0157	88	.9808	38	1.0134	98	.9777	38	1.0111	98	.9814	38	1.0089	188	.9513	225	.9410	485	.8610
39	1.0171	84	.9812	39	1.0150	89	.9801	39	1.0128	99	.9771	39	1.0106	99	.9809	39	1.0085	189	.9509	230	.9393	490	.8595
40	1.0162	85	.9804	40	1.0143	90	.9794	40	1.0121	100	.9766	40	1.0101	100	.9804	40	1.0081	190	.9506	235	.9376	495	.8581
41	1.0154	86	.9796	41	1.0136	91	.9788	41	1.0115	101	.9760	41	1.0096	101	.9799	41	1.0077	191	.9502	240	.9360	500	.8568
42	1.0146	87	.9789	42	1.0129	92	.9781	42	1.0109	102	.9754	42	1.0090	102	.9794	42	1.0073	192	.9498	245	.9343	505	.8554
43	1.0138	88	.9781	43	1.0122	93	.9774	43	1.0103	103	.9749	43	1.0086	103	.9789	43	1.0068	193	.9495	250	.9327	510	.8540
44	1.0130	89	.9773	44	1.0114	94	.9768	44	1.0097	104	.9743	44	1.0081	104	.9785	44	1.0064	194	.9491	255	.9310	515	.8526
45	1.0121	90	.9766	45	1.0107	95	.9761	45	1.0091	105	.9737	45	1.0076	105	.9780	45	1.0060	195	.9488	260	.9294	520	.8512
				46	1.0100	96	.9754	46	1.0085	106	.9731	46	1.0070	106	.9775	46	1.0056	196	.9484	265	.9277	525	.8498
				47	1.0093	97	.9748	47	1.0079	107	.9726	47	1.0065	107	.9770	47	1.0052	197	.9480	270	.9261	530	.8485
				48	1.0086	98	.9741	48	1.0073	108	.9720	48	1.0060	108	.9766	48	1.0048	198	.9477	275	.9245	535	.8471
				49	1.0079	99	.9734	49	1.0066	109	.9714	49	1.0055	109	.9761	49	1.0044	199	.9473	280	.9228	540	.8457
				50	1.0072	100	.9728	50	1.0060	110	.9709	50	1.0050	110	.9756	50	1.0040	200	.9470	285	.9212	545	.8444
								51	1.0054	111	.9703	51	1.0045	111	.9751	51	1.0036	201	.9466	290	.9196	550	.8430
								52	1.0048	112	.9697	52	1.0040	112	.9747	52	1.0032	202	.9462	295	.9180		
								53	1.0042	113	.9692	53	1.0035	113	.9742	53	1.0028	203	.9459				
								54	1.0036	114	.9686	54	1.0030	114	.9737	54	1.0024	204	.9455				
								55	1.0030	115	.9681	55	1.0025	115	.9732	55	1.0020	205	.9452				
								56	1.0024	116	.9675	56	1.0020	116	.9728	56	1.0016	206	.9448				
								57	1.0018	117	.9669	57	1.0015	117	.9723	57	1.0012	207	.9445				
								58	1.0012	118	.9664	58	1.0010	118	.9718	58	1.0008	208	.9441				
								59	1.0006	119	.9658	59	1.0005	119	.9713	59	1.0004	209	.9437				
								60	1.0000	120	.9653	60	1.0000	120	.9708	60	1.0000	210	.9434				
																61	.9996	211	.9430				
																62	.9992	212	.9427				
																63	.9988	213	.9423				
																64	.9984	214	.9420				
																65	.9980	215	.9416				
																66	.9976	216	.9413				
																67	.9972	217	.9409				
																68	.9968	218	[illegible]				
																69	.9964	219	[illegible]				
																70	.9960	[illegible]	[illegible]				
																71	.9956	[illegible]	[illegible]				
																[illegible]	.9953	[illegible]	[illegible]				
																[illegible]	.9948	[illegible]	[illegible]				
																[illegible]	.9944	[illegible]	[illegible]				
																[illegible]	[illegible]	[illegible]	[illegible]				
																[illegible]	[illegible]	[illegible]	[illegible]				
																[illegible]	[illegible]	[illegible]	[illegible]				
																[illegible]	[illegible]	[illegible]	[illegible]				
																[illegible]	[illegible]	[illegible]	[illegible]				
																[illegible]	[illegible]	[illegible]	[illegible]				
																[illegible]	[illegible]	[illegible]	[illegible]				
																[illegible]	[illegible]	[illegible]	[illegible]				

TABLE XC—*Continued*

DELBRIDGE'S VOLUME CORRECTION MULTIPLIERS

Part			Part B				Part C				Part D				Part E				Part F			
…ing to … and lig… co-efficier… of 0.00		…es of … Based … expan-	Applying to gravities of 78.9-65.0. Based on co-efficient of expansion of 0.0007.				Applying to gravities 64.9-51.0. Based on co-efficient of expansion 0.0006.				Applying to gravities 50.9-35.0. Based on co-efficient of expansion 0.0005.				Applying to gravities heavier than 35.0. Based on co-efficient of expansion 0.0004.				Applying to Pitches. Based on co-efficient of expansion 0.00038.			
Multi-plier	Degree	Multi-plier	Degree	Multi-plier	Degree	Multi-plier	Degree	Multi-plier	Degree	Multi-plier	Degree	Multi-plier	Degree	Multi-plier	Degree	Multi-plier	Degree	Multi-plier	Degree	Multi-plier	Degree	Multi-plier
															83	.9909	233	.9353				
															84	.9905	234	.9349				
															85	.9901	235	.9346				
															86	.9897	236	.9342				
															87	.9893	237	.9339				
															88	.9889	238	.9335				
															89	.9885	239	.9332				
															90	.9881	240	.9328				
															91	.9878	241	.9325				
															92	.9874	242	.9321				
															93	.9870	243	.9318				
															94	.9866	244	.9315				
															95	.9862	245	.9311				
															96	.9858	246	.9307				
															97	.9854	247	.9304				
															98	.9850	248	.9301				
															99	.9846	249	.9297				
															100	.9843	250	.9294				
															101	.9839	251	.9290				
															102	.9835	252	.9287				
															103	.9831	253	.9283				
															104	.9827	254	.9280				
															105	.9823	255	.9276				
															106	.9819	256	.9273				
															107	.9815	257	.9269				
															108	.9812	258	.9266				
															109	.9808	259	.9263				
															110	.9804	260	.9259				
															111	.9800	261	.9256				
															112	.9796	262	.9252				
															113	.9792	263	.9249				
															114	.9789	264	.9245				
															115	.9785	265	.9242				
															116	.9781	266	.9239				
															117	.9777	267	.9235				

118	.9773	268	.9232
119	.9769	269	.9228
120	.9766	270	.9225
121	.9762	271	.9222
122	.9758	272	.9218
123	.9754	273	.9215
124	.9750	274	.9211
125	.9746	275	.9208
126	.9743	276	.9205
127	.9739	277	.9201
128	.9735	278	.9198
129	.9731	279	.9194
130	.9728	280	.9191
131	.9724	281	.9188
132	.9720	282	.9184
133	.9716	283	.9181
134	.9713	284	.9178
135	.9709	285	.9174
136	.9705	286	.9171
137	.9701	287	.9168
138	.9697	288	.9164
139	.9694	289	.9161
140	.9690	290	.9157
141	.9686	291	.9154
142	.9682	292	.9151
143	.9679	293	.9147
144	.9675	294	.9144
145	.9671	295	.9141
146	.9667	296	.9137
147	.9664	297	.9134
148	.9660	298	.9131
149	.9656	299	.9127
150	.9653	300	.9124

TABLE XCI

CORRESPONDING SPECIFIC GRAVITIES AND DEGREES A. P. I.

$$\text{Degrees A. P. I.} = \frac{141.5}{\text{Sp. Gr.}} - 131.5$$

Sp. Gr.	Degrees A. P. I.	Lbs. per Gal.
0.600	104.3	4.993
0.610	100.4	5.076
0.620	96.7	5.160
0.630	93.1	5.243
0.640	90.4	5.326
.650	86.1	5.410
.660	82.8	5.493
.670	79.6	5.577
.680	76.5	5.660
.690	73.5	5.743
.700	70.6	5.827
.710	67.7	5.910
.720	65.0	5.994
.730	62.3	6.077
.740	59.7	6.160
.750	57.1	6.244
.760	54.6	6.327
.770	52.2	6.410
.780	49.6	6.494
.790	47.6	6.577
.800	45.3	6.661
.810	43.1	6.744
.820	41.0	6.827
.830	38.9	6.911
.840	36.9	6.994
.850	34.9	7.078
.860	33.0	7.161
.870	31.1	7.244
.880	29.2	7.328
.890	27.4	7.411
.900	25.7	7.494
.910	23.9	7.578
.920	22.3	7.661
.930	20.6	7.745
.940	19.0	7.828
.950	17.4	7.911
.960	15.8	7.995
.970	14.3	8.078
.980	12.8	8.162
.990	11.4	8.245
1.000	10.0	8.328

TABLE XCII

CORRESPONDING DEGREES A. P. I. AND SPECIFIC GRAVITIES

$$S.\ G. = \frac{141.5}{131.5 + A.\ P.\ I.^\circ}$$

Deg. A. P. I.	Sp. Gr.	Lbs. per Gal.	Deg. A. P. I.	Sp. Gr.	Lbs. per Gal.
10.	1.0000	8.331	51.	.7753	6.459
11.	.9930	8.273	52.	.7711	6.424
12.	.9861	8.215	53.	.7669	6.389
13.	.9792	8.158	54.	.7628	6.355
14.	.9725	8.102	55.	.7587	6.321
15.	.9659	8.047	56.	.7547	6.287
16.	.9593	7.992	57.	.7507	6.254
17.	.9529	7.939	58.	.7467	6.221
18.	.9465	7.885	59.	.7428	6.188
19.	.9402	7.833	60.	.7389	6.156
20.	.9340	7.781	61.	.7351	6.124
21.	.9279	7.730	62.	.7313	6.092
22.	.9218	7.679	63.	.7275	6.061
23.	.9159	7.630	64.	.7238	6.030
24.	.9100	7.581	65.	.7201	5.999
25.	.9042	7.533	66.	.7165	5.969
26.	.8984	7.485	67.	.7128	5.938
27.	.8927	7.437	68.	.7093	5.909
28.	.8871	7.390	69.	.7057	5.879
29.	.8816	7.345	70.	.7022	5.850
30.	.8762	7.300	71.	.6987	5.821
31.	.8708	7.255	72.	.6953	5.793
32.	.8654	7.210	73.	.6919	5.764
33.	.8602	7.166	74.	.6886	5.737
34.	.8550	7.123	75.	.6852	5.708
35.	.8498	7.080	76.	.6819	5.681
36.	.8448	7.038	77.	.6787	5.654
37.	.8398	6.996	78.	.6754	5.627
38.	.8348	6.955	79.	.6722	5.600
39.	.8299	6.914	80.	.6690	5.573
40.	.8251	6.874	81.	.6659	5.548
41.	.8203	6.834	82.	.6628	5.522
42.	.8156	6.795	83.	.6597	5.496
43.	.8109	6.756	84.	.6566	5.470
44.	.8063	6.717	85.	.6536	5.445
45.	.8017	6.679	86.	.6506	5.420
46.	.7972	6.641	87.	.6476	5.395
47.	.7927	6.604	88.	.6446	5.370
48.	.7883	6.567	89.	.6417	5.346
49.	.7839	6.531	90.	.6388	5.322
50.	.7796	6.495	....	.....	.....

TABLE XCIII

Corresponding Specific Gravities and Degrees Baumé

$$\text{Bé.}^\circ_L = \frac{140}{\text{Sp. Gr. } 60^\circ \text{ F.}/60^\circ \text{ F.}} - 130$$

Sp. Gr. 60°/60° F.	Deg. Bé. (modulus 140)	Lbs. per Gal.
.600	103.33	4.993
.610	99.51	5.076
.620	95.81	5.160
.630	92.22	5.243
.640	88.75	5.326
.650	85.38	5.410
.660	82.12	5.493
.670	78.96	5.577
.680	75.88	5.660
.690	72.90	5.743
.700	70.00	5.827
.710	67.18	5.910
.720	64.44	5.994
.730	61.78	6.077
.740	59.19	6.160
.750	56.67	6.244
.760	54.21	6.327
.770	51.82	6.410
.780	49.49	6.494
.790	47.22	6.577
.800	45.00	6.661
.810	42.84	6.744
.820	40.73	6.827
.830	38.68	6.911
.840	36.67	6.994
.850	34.71	7.078
.860	32.79	7.161
.870	30.92	7.244
.880	29.09	7.328
.890	27.30	7.411
.900	25.56	7.494
.910	23.85	7.578
.920	22.17	7.661
.930	20.54	7.745
.940	18.94	7.828
.950	17.37	7.911
.960	15.83	7.995
.970	14.33	8.078
.980	12.86	8.162
.990	11.41	8.245
1.000	10.00	8.328

TABLE XCIV

CORRESPONDING DEGREES BAUMÉ AND SPECIFIC GRAVITIES

$$\text{Sp. Gr.} = \frac{140}{130 + \text{Bé.}^\circ_L}$$

Deg. Bé.	Sp. Gr.	Lbs. per Gal.	Deg. Bé.	Sp. Gr.	Lbs. per Gal.
10	1.0000	8.328	56	.7527	6.266
11	.9929	8.269	57	.7487	6.233
12	.9859	8.211	58	.7447	6.199
13	.9790	8.153	59	.7407	6.166
14	.9722	8.096	60	.7368	6.134
15	.9655	8.041	61	.7330	6.102
16	.9589	7.986	62	.7292	6.070
17	.9524	7.931	63	.7254	6.038
18	.9459	7.877	64	.7216	6.007
19	.9396	7.825	65	.7179	5.976
20	.9333	7.772	66	.7143	5.946
21	.9272	7.721	67	.7107	5.916
22	.9211	7.670	68	.7071	5.886
23	.9150	7.620	69	.7035	5.856
24	.9091	7.570	70	.7000	5.827
25	.9032	7.522	71	.6965	5.798
26	.8974	7.473	72	.6931	5.769
27	.8917	7.425	73	.6897	5.741
28	.8861	7.378	74	.6863	5.712
29	.8805	7.332	75	.6829	5.685
30	.8750	7.286	76	.6796	5.657
31	.8696	7.241	77	.6763	5.629
32	.8642	7.196	78	.6731	5.602
33	.8589	7.152	79	.6699	5.576
34	.8537	7.108	80	.6667	5.549
35	.8485	7.065	81	.6635	5.522
36	.8434	7.022	82	.6604	5.497
37	.8383	6.980	83	.6573	5.471
38	.8333	6.939	84	.6542	5.445
39	.8284	6.898	85	.6512	5.420
40	.8235	6.857	86	.6482	5.395
41	.8187	6.817	87	.6452	5.370
42	.8140	6.777	88	.6422	5.345
43	.8092	6.738	89	.6393	5.320
44	.8046	6.699	90	.6364	5.296
45	.8000	6.661	91	.6335	5.272
46	.7955	6.623	92	.6306	5.248
47	.7910	6.586	93	.6278	5.225
48	.7865	6.548	94	.6250	5.201
49	.7821	6.511	95	.6222	5.178
50	.7778	6.476	96	.6195	5.155
51	.7735	6.440	97	.6167	5.132
52	.7692	6.404	98	.6140	5.110
53	.7650	6.369	99	.6114	5.088
54	.7609	6.334	100	.6087	5.066
55	.7568	6.300			

Reference—P. 57, Circular 57, U. S. Bureau of Standards.

TABLE XCV

Specific Gravity Conversions

The first column shows Specific Gravity at temperature 60°/60° F. The other columns show the corrections to be applied to indications of an hydrometer, standardized at 60°/60° F., to convert it to the standard temperature shown at top of each column.

To convert indications of hydrometers standardized at other than 60°/60° F., add the algebraic difference between the correction for the temperature of standardization desired and the correction for the temperature of standardization of the hydrometer with which the reading is taken. Example: Reading of a hydrometer standardized at 20°/4° C. is 1.550; to convert to value standardized at 20°/20° C. add .0027, making 1.5527.

Sp. Gr. 60°/60° F. or 15.56°/15.56° C.	Corrections to be added				
	15°/4° C.	20°/4° C.	20°/20° C.	17½°/17½° C.	25°/25° C.
0.650	−0.0006	−0.0007	+0.0005	+0.0002	+0.0012
0.675	−0.0006	−0.0007	+0.0005	+0.0002	+0.0012
0.700	−0.0007	−0.0008	+0.0005	+0.0002	+0.0012
0.750	−0.0007	−0.0008	+0.0005	+0.0002	+0.0013
0.800	−0.0007	−0.0008	+0.0005	+0.0002	+0.0013
0.825	−0.0008	−0.0009	+0.0006	+0.0002	+0.0014
0.875	−0.0008	−0.0009	+0.0006	+0.0002	+0.0015
0.900	−0.0009	−0.0010	+0.0006	+0.0002	+0.0016
0.925	−0.0009	−0.0010	+0.0007	+0.0002	+0.0016
1.000	−0.0009	−0.0011	+0.0007	+0.0003	+0.0017
1.050	−0.0010	−0.0011	+0.0007	+0.0003	+0.0018
1.075	−0.0010	−0.0011	+0.0007	+0.0003	+0.0019
1.100	−0.0010	−0.0012	+0.0008	+0.0003	+0.0019
1.150	−0.0011	−0.0012	+0.0008	+0.0003	+0.0020
1.200	−0.0011	−0.0013	+0.0008	+0.0003	+0.0021
1.225	−0.0012	−0.0013	+0.0009	+0.0003	+0.0021
1.250	−0.0012	−0.0013	+0.0009	+0.0004	+0.0022
1.300	−0.0012	−0.0014	+0.0009	+0.0004	+0.0023
1.325	−0.0012	−0.0014	+0.0009	+0.0004	+0.0024
1.350	−0.0013	−0.0014	+0.0010	+0.0004	+0.0024
1.375	−0.0013	−0.0015	+0.0010	+0.0004	+0.0024
1.400	−0.0013	−0.0015	+0.0010	+0.0004	+0.0025
1.450	−0.0014	−0.0015	+0.0010	+0.0004	+0.0025
1.475	−0.0014	−0.0016	+0.0010	+0.0004	+0.0026
1.500	−0.0014	−0.0016	+0.0011	+0.0004	+0.0026
1.550	−0.0015	−0.0016	+0.0011	+0.0004	+0.0027
1.575	−0.0015	−0.0017	+0.0011	+0.0004	+0.0027
1.600	−0.0015	−0.0017	+0.0011	+0.0004	+0.0028
1.625	−0.0015	−0.0017	+0.0011	+0.0005	+0.0028
1.650	−0.0016	−0.0017	+0.0012	+0.0005	+0.0029
1.700	−0.0016	−0.0018	+0.0012	+0.0005	+0.0030
1.725	−0.0016	−0.0018	+0.0012	+0.0005	+0.0031
1.775	−0.0017	−0.0019	+0.0012	+0.0005	+0.0031
1.800	−0.0017	−0.0019	+0.0013	+0.0005	+0.0032
1.850	−0.0017	−0.0019	+0.0013	+0.0005	+0.0032
1.900	−0.0018	−0.0020	+0.0013	+0.0005	+0.0033
1.925	−0.0018	−0.0020	+0.0014	+0.0005	+0.0033
1.950	−0.0018	−0.0021	+0.0014	+0.0006	+0.0034
2.000	−0.0019	−0.0021	+0.0014	+0.0006	+0.0035

From Tycos Mineral Oil Tables, pp. 58-9.

TABLE XCVI

REFRACTIVE INDICES OF SEVERAL PETROLEUMS [18]

Petroleum	Gravity	Color	Refractive Indices at 20° C.
Cabin Creek, W. Va.	48.0	Yellow	1.4468
Montana *	46.4	Dark green	1.4350
Riverton, Wyo.	46.2	White	1.4410
Bull Bayou, La.*	40.8	Green	1.4549
Corning, Ohio *	39.9	Greenish brown	1.4550
Cushing, Okla.*	39.4	Dark green	1.4540
Homer, La.*	38.9	Very dark green	1.4430
Osage, Okla.*	36.6	Dark green	1.4650
Bixby, Okla.*	35.7	Dark green	1.4485

The crudes marked * were too dark to test alone and the refractive index was obtained by testing a blend of the crude and kerosene, then calculating the refractive index of the crude by the following table or formula:

$$R = \frac{100 \times R_1 - (P_2 \times R_2)}{P}$$

R = Refractive index of crude.
R_1 = Refractive index of blend.
R_2 = Refractive index of kerosene.
P = Per cent of crude in blend.
P_2 = Per cent of kerosene in blend.

[18] Francis, C. K., and Bennett, H. T., *Pet. Age,* May, 1921, 134-5.

TABLE XCVII

REFRACTIVE INDICES AND TESTS OF GASOLINES AND NAPHTHAS FROM BLENDS OF CUSHING AND BIXBY CRUDES [19]

Product *	Deg. Bé.	Initial	Dry	Refractive Index at 20° C.
Gasoline	64.9	96	446	1.4155
Gasoline	63.3	112	402	1.4052
Gasoline	62.4	128	380	1.4120
Gasoline	62.1	120	394	1.4122
Gasoline	61.9	130	402	1.4150
Compression Gasoline *	61.4	102	456	1.4229
Gasoline	60.9	115	418	1.4138
"Cracked" Gasoline	60.0	146	418	1.4148
Compression Gasoline	59.9	122	448	1.4228
Gasoline	59.9	110	452	1.4221
Gasoline	59.8	120	436	1.4153
Gasoline	59.1	125	448	1.4221
Gasoline	58.8	115	456	1.4235
Compression Gasoline **	58.7	110	451	1.4270
Gasoline	58.2	141	448	1.4154
Gasoline	58.0	150	416	1.4200
Gasoline	57.9	136	416	1.4199
Gasoline	55.9	140	440	1.4225
Naphtha	53.9	161	436	1.4259
Naphtha	53.7	174	478	1.4270
Naphtha	52.8	152	480	1.4321
Naphtha	52.5	192	464	1.4290
Benzine	56.7	150	515	1.4223
Benzine	47.5	168	615	1.4402
Pressure Distillate	48.4	136	548	1.4430
Pressure Distillate	48.3	136	550	1.4442

* The color of the gasoline and naphtha was water white.

** The compression gasoline was made from still-gases from crude, benzine, and pressure stills.

[19] Francis, C. K., & Bennett, H. T., *Pet. Age*, May, 1921, 134-5.

TABLE XCVIII

REFRACTIVE INDICES AND TESTS OF KEROSENE AND GAS OIL FROM BLENDS OF CUSHING AND BIXBY CRUDES [20]

Product	Degrees Baumé	Flash	Fire	Lovibond Color	Refractive Index at 20° C.
Prime White Distillate.......	44.0	122	142	W.W. —2.2	1.4479
Prime White Distillate.......	43.7	126	146	W.W. —6.5	1.4478
Prime White Distillate.......	43.3	119	140	W.W. —1.5	1.4485
Kerosene	42.7	136	158	W.W. —2.2	1.4494
Kerosene	42.5	130	150	W.W. —2.2	1.4510
Kerosene	41.8	104	130	W.W. —2.2	1.4530
Gas Oil	32.3	...	...	....	1.4790

TABLE XCIX

REFRACTIVE INDICES OF PRODUCTS FROM MID-CONTINENT PETROLEUMS [21]

	Bixby, Okla.		Cushing, Okla.		Ranger, Texas	
	Deg. Bé.	Refractive Index 20° C.	Deg. Bé.	Refractive Index 20° C.	Deg. Bé.	Refractive Index 20° C.
Crude	35.7	1.4485 *	38.9	1.4568 *	37.5	1.4630 *
Benzine	56.7	1.4188	57.2	1.4225	54.5	1.4263
Gas Oil	35.9	1.4690	35.7	1.4725	35.9	1.4690
Wax Distillate......	32.6	1.4831	32.6	1.5023	32.9	1.4865
Kerosene	42.5	1.4502	42.1	1.4518	42.1	1.4510

* Calculated.

[20] Francis, C. K., & Bennett, H. T., *Pet. Age,* May, 1921, 134-5.
[21] Francis, C. K., & Bennett, H. T., *Pet. Age,* May, 1921, 134-5.

TABLE C

HEATS OF COMBUSTION AND DENSITIES OF PETROLEUMS[22]

Description of oil	Sp. Gr at 0° C.	° Bé.	Chemical composition C	H_2	O_2	Co-efficient of expansion	Calorific power Cal. per gram	B.t.u. per lb.
Heavy petroleum from W. Va.	0.873	30.0	83.5	13.3	3.2	0.00072	10,180	18,324
Light petroleum from W. Va.	0.8412	37.5	84.3	14.1	1.6	0.000839	10,223	18,401
Light petroleum from Penn.	0.816	41.5	82.0	14.8	3.2	0.00084	9,963	17,933
Heavy petroleum from Penn.	0.886	28.0	84.9	13.7	1.4	0.000721	10,672	19,210
American petroleum	0.820	40.5	83.4	14.7	1.9	0.000868	9,771	17,588
Petroleum from								
Parma	0.786	48.0	84.0	13.4	1.8	0.000706	10,121	18,218
Pechelbronn	0.912	23.5	86.9	11.8	1.3	0.000767	9,708	17,474
"	0.892	27.0	85.7	12.0	2.3	0.000793	10,020	18,036
Schwabweiler	0.861	32.5	86.2	13.3	0.5	0.000858	10,458	18,824
"	0.829	39.0	79.5	13.6	6.9	0.000843	......	......
Hanover, Eddesse	0.892	27.0	80.4	12.7	6.9	0.000772	......	......
Hanover, Wietze	0.955	16.5	86.2	11.4	2.4	0.000641	......	......
East Galacia	0.870	31.0	82.2	12.1	5.7	0.000813	10,005	18,009
West Galacia	0.885	28.0	85.3	12.6	2.1	0.000775	10,231	18,416
Shale-oil from Ardeche, Vagnas	0.911	23.5	80.3	11.5	8.2	0.000896	9,046	16,283
Coal-tar from Paris gas-works	1.044	....	82.0	7.6	10.4	0.000743	8,916	16,049
Petroleum from Bala-khani	0.822	40.75	87.4	12.5	0.1	0.000817	11,700	21,060
Light petroleum from Baku	0.884	28.5	86.3	13.6	0.1	0.000724	11,460	20,628
Petroleum residues from the Baku factories	0.928	21.0	87.1	11.7	1.2	0.00091	10,700	19,260
Heavy petroleum from Baku	0.938	19.0	86.6	12.3	1.1	0.000681	10,800	19,440
Petroleum from Java	0.923	21.5	87.1	12.0	0.9	0.000769	10,831	19,496
Heavy oil of pine (Landes)	0.985	12.0	87.7	10.4	2.5	0.000685	10,081	18,146

[22] Engler-Hofer, "Das Erdol," 1913 Ed., 161.

TABLE CI

HEATS OF COMBUSTION AND DENSITIES OF PETROLEUMS AND PETROLEUM PRODUCTS[23]

No.	Sp. gr. 15°/15°	Bé. deg.	Cal. per gram	B.t.u. per lb.	B.t.u. calculated	Percentage error	Description
1	0.7100	67.2	11,733	21,120	20,938	−0.91	Gasoline
2	0.7175	65.1	11,327	20,389	20,854	+2.33	"
3	0.7200	64.4	11,404	20,527	20,726	+0.99	"
4	0.7709	51.6	11,132	20,038	20,314	+1.38	*
5	0.7830	48.8	11,121	20,018	20,206	+0.92	Kerosene
6	0.7850	48.35	11,119	20,014	20,194	+0.89	California refined
7	0.7945	46.2	11,128	20,030	20,098	+0.33	West Va. crude
8	0.7950	46.1	11,186	20,135	20,094	−0.20	Kerosene
9	0.7964	45.8	11,242	20,236	20,082	−0.76	*
10	0.8048	44.0	11,149	20,068	20,010	−0.29	Ohio crude
11	0.8059	43.7	11,143	20,057	19,998	−0.29	Penna. crude
12	0.8080	43.2	11,001	19,802	19,979	+0.88	California refined
13	0.8103	42.8	11,090	19,963	19,962	±0.00	Kansas refined
14	0.8237	40.0	10,981	19,766	19,850	+0.42	West Va. crude
15	0.8248	39.7	11,015	19,827	19,838	+0.05	California refined
16	0.8261	39.5	11,123	20,021	19,830	−0.95	West Va. crude
17	0.8321	38.2	10,972	19,757	19,778	+0.11	*
18	0.8324	38.2	10,990	19,782	19,778	−0.02	Penna. crude
19	0.8418	36.3	10,950	19,710	19,702	−0.04	Ohio crude
20	0.8421	36.25	10,997	19,795	19,698	−0.48	Indian Ter.
21	0.8436	36.0	11,069	19,924	19,690	−1.17	*
22	0.8466	35.4	10,936	19,685	19,666	−0.09	Indian Ter.
23	0.8500	34.7	10,953	19,715	19,638	−0.38	California refined
24	0.8510	34.5	10,958	19,724	19,630	−0.47	Kansas crude
25	0.8514	34.45	10,945	19,701	19,630	−0.35	*
26	0.8534	34.05	10,991	19,784	19,610	−0.86	*
27	0.8580	33.2	10,772	19,389	19,578	+0.95	Kansas crude
28	0.8597	32.8	10,766	19,379	19,562	+0.95	Illinois crude
29	0.8616	32.5	10,967	19,741	19,550	−0.95	*
30	0.8640	32.05	10,867	19,555	19,530	−0.12	California refined
31	0.8648	31.9	10,920	19,656	19,526	−0.65	Penn. fuel oil
32	0.8660	31.65	10,864	19,555	19,516	−0.19	Fuel oil
33	0.8670	31.5	10,850	19,530	19,510	−0.10	Penn. fuel oil
34	0.8690	31.1	10,852	19,534	19,494	−0.20	Indian Ter.
35	0.8708	30.8	10,919	19,654	19,482	−0.86	*
36	0.8712	30.7	10,879	19,614	19,478	−0.68	*
37	0.8745	30.1	10,752	19,354	19,454	+0.50	Kansas crude
38	0.8773	29.6	10,794	19,429	19,434	+0.03	Penn. fuel oil
39	0.8800	29.0	10,804	19,447	19,410	−0.18	Kansas crude
40	0.8807	29.0	10,797	19,435	19,410	−0.47	*
41	0.8810	28.9	10,797	19,435	19,406	−0.15	
42	0.8820	28.75	10,913	19,643	19,400	−1.22	*
43	0.8828	28.7	10,694	19,249	19,396	+0.73	Kansas crude
44	0.8833	28.5	10,819	19,474	19,390	−0.42	*
45	0.8860	28.0	10,808	19,454	19,370	−0.42	Indian Ter.
46	0.8862	28.0	10,762	19,372	19,370	−0.01	*
47	0.8900	27.3	10,788	19,418	19,342	−0.39	Indian Ter.

* Obtained by fractional distillation of commercial fuel or gas oils—Nos. 4, 25, 36, 44 and 52 were the successive fifths from one sample; Nos. 9, 21, 26, 29, and 42 from a second; Nos. 17, 35, 40, 46 and 50 from a third.

[23] Sherman, H. C., & Kropff, A. H., *J. Am. Chem. Soc.*, 30 (1908), 1628-9.

TABLE CI—*Continued*

No.	Sp. gr. 15°/15°	Bé. deg.	Cal. per gram	B.t.u. per lb.	B.t.u. calculated	Percentage error	Description
48..........	0.8914	27.1	10,690	19,242	19,332	+ 0.45	Texas crude
49..........	0.8970	26.1	10,753	19,355	19,294	— 0.31	
50..........	0.9007	25.4	10,755	19,359	19,267	— 0.47	*
51..........	0.9050	24.7	10,682	19,228	19,238	+ 0.05	
52..........	0.9065	24.45	10,751	19,352	19,228	— 0.63	*
53..........	0.9066	24.4	10,605	19,089	19,226	+ 0.69	Kansas crude
54..........	0.9087	24.1	10,712	19,282	19,213	— 0.35	
55..........	0.9114	23.6	10,724	19,303	19,194	— 0.55	Kansas crude
56..........	0.9137	23.2	10,571	19,028	19,178	+ 0.76	Texas crude
57..........	0.9153	22.95	10,692	19,246	19,168	— 0.39	Texas crude
58..........	0.9155	22.9	10,560	19,008	19,166	+ 0.80	Texas crude
59..........	0.9158	22.9	10,318	18,572	19,166	+ 2.58	California crude
60..........	0.9170	22.7	10,613	19,103	19,157	+ 0.28	Fuel oil
61..........	0.9179	22.5	10.433	18,779	19,150	+ 1.94	California crude
62..........	0.9182	22.5	10,547	18,985	19,149	+ 0.83	California crude
63..........	0.9336	20.0	10,600	19,080	19,048	— 0.16	Texas crude
64..........	0.9644	15.2	10,327	18,589	18,858	+ 1.42	California crude

* Obtained by fractional distillation of commercial fuel or gas oils—Nos. 4, 25, 36, 44 and 52 were the successive fifths from one sample; Nos. 9, 21, 26, 29, and 42 from a second; Nos. 17, 35, 40, 46 and 50 from a third.

It will be seen that throughout the range of oils included in the table there is a general tendency toward a fairly regular decrease in calorific power as the specific gravity increases and the Baumé numbers decrease.

In the cases in which an approximate estimate of the calorific power is most likely to be useful, the expression of density in terms of the Baumé scale and of calorific power in British thermal units per pound will probably be most common.[23a] By grouping the samples falling within certain limits of Baumé density and plotting the average figures, it was found that the approximate average relation between Baumé density and calorific power in B.t.u. may be expressed as follows:

$$\text{B.t.u.} = 18{,}650 + 40\ (\text{Baumé} - 10).$$

This formula was then applied to the data of the individual samples. In the column headed "B.t.u. calculated" and "percentage error" are given for each sample the calculated British thermal units and the percentage difference between the calculated and the determined values.

It will be seen that the difference between the calorific power as determined in the bomb calorimeter and as calculated from the formula here proposed is usually small. In only one-ninth of the cases is the difference greater than 1 per cent, in only one-thirtieth is it greater than 2 per cent, in no case is it as great as 3 per cent.

[23a] It should perhaps be noted that the heavier oils with lower calorific power per gram or per pound would show higher calorific power *per gallon* than the light oils.

TABLE CII

Specific Heats of Crude Petroleums [24]

	Specific Gravity	Specific Heat
Pennsylvania	0.8095	.5000
Berea Grit	0.7939	.4690
Japanese	0.8622	.4532
Texas (Lucas well)	0.9200	.4315
Russian	0.9079	.4355
Wyoming	0.8816	.4323
California	0.9600	.3980
Texas	0.9466	.4009
Ohio	......	.4951
Commercial Gasoline	......	.5135

Note: The specific heat of the hydrocarbons of several series are also given in this article.

TABLE CIII

Specific Heats of California Petroleums [25]

Twelve samples of oil were used. They were tested for water, low boiling fractions and asphalt. The results of the analysis of these oils, as well as the specific heats found, are given below.

	Distillate Percentages					Specific Heats at 20° C.
	Water	0-150° C.	150-300° C.	300° to Asphalt	Asphalt	
1	0	....	.....	....	.....	0.3999
2	0.33	....	.....	....	.....	0.4143
3	0.52	....	.....	....	.....	0.4389
4	7.0	5.7	23.14	32.1	31.7	0.5016
5	1.3	0	37.4	30.0	30.91	0.4788
6	0	35.6	54.1	4.2	6.2	0.4804
7	0	8.1	27.3	39.7	23.5	0.4474
8	0	25.8	43.3	22.1	7.0	0.4832
9	0	0	12.3	48.7	36.3	0.4419
10	0	0	22.5	42.3	34.7	0.4553
11	6.2	0	30.9	22.6	39.9	0.4559
12	0	0	34.1	30.2	35.4	0.4491

The oils 1, 2, and 3 were oils containing only the fractions from 300° C. up.

[24] Mabery, C. F., & Goldstein, A. H., *Proc. Am. Acad. Arts Sci.*, 37 (1902), 546.

[25] Wales, H. E., *J. Ind. Eng. Chem.*, 6 (1914), 728.

TABLE CIV

Specific Heats of Petroleum Products [26]

MOTOR SPIRIT

	Sp. Gr. (at 15° C.)	Sp. Ht.	Sp. Gr. × Sp. Heat
Anglo-American Oil Company, Ltd.—Heavy ("Taxibus")	0.7375	0.465	0.343
Anglo-American Oil Company, Ltd.—Light ("Pratt's Perfection")	0.7240	0.483	0.350
Asiatic Petroleum Company, Ltd.—"Shell," Heavy ("760 Benzine")	0.7675	0.450	0.346
Asiatic Petroleum Company, Ltd.—"Shell," Light ("720 Benzine")	0.7215	0.490	0.352

KEROSENE

Anglo-American Oil Company, Ltd.—Water white	0.799	0.457	0.365
Anglo-American Oil Company, Ltd.—Standard white	0.8035	0.450	0.362
Russian	0.8248	0.435	0.358
Roumanian	0.8127	0.444	0.361
Shale oil (Young's Paraffin oil)	0.804	0.472	0.379

FUEL OIL

Russian	0.914	0.448	.....
Burma	0.897	0.433	.....
Texas	0.927	0.436	.....

TABLE CV

Specific Heats of Fractions from Baku Petroleum [27]

Temperature ° C.	I 100–165° 0.7524	II 165–170° 0.8045	III 170–175° 0.8089	IV 235–240° 0.8432	Lubricating Oil 0.869/19.5°	Lubricating Oil 0.9095/20°
40–35	0.505	0.501	0.488	0.465	0.479	0.571
35–30	0.490	0.489	0.480	0.463	0.475	0.566
30–25	0.475	0.481	0.469	0.460	0.471	0.559
25–20	0.469	0.474	0.459	0.459	0.463	0.550
20–15	0.459	0.469	0.457	0.449	0.452	0.550
40–15	0.479	0.483	0.470	0.459	0.468	0.559

, Redwood's "Treatise on Petroleum," 4th ed., 1922, 279.
ˋ^ly. J., 253 (1884), 949.

TABLE CVI

SPECIFIC HEATS OF DISTILLATES[28]

	Specific Heat in B.t.u. per lb.
Gasoline—89° Bé.	0.580
Gasoline—65° Bé.	0.569
Naphtha—56° Bé.	0.510
Kerosene—43° Bé.	0.499

TABLE CVII

SPECIFIC HEATS OF PETROLEUMS AND PETROLEUM PRODUCTS[29]

CADDO PETROLEUM AND ITS PRODUCTS

		Gravity ° Bé.	52° F.	102° F.	126° F.	155° F.	176° F.	212° F.
c — c	Crude oil..	40.6	......	0.5003	0.5283	......	......	......
o — o	Distillates:							
	I	67.2	0.4933	0.5382	0.5620	......	......	......
	II	60.8	......	0.5217	0.5462	......	......	......
	III	48.9	......	0.5083	0.5326	......	......	......
	IV	41.2	0.4688	0.5074	0.5228	......	0.5591	......
x — x	Paraffin— m.p. 125° F.	....	......	......	0.5700	0.5798	0.5974	0.6307
G — G	Gas oil ...	27.1	......	0.4554	0.5006	......	0.5432	......

HYDROCARBONS AT 25° C.

C_6 Hexane	0.5272
C_7 Heptane	0.5074
C_{10} Decane	0.5021
C_{16} Hexadecane	0.4957

OKLAHOMA PETROLEUM AND ITS PRODUCTS

		Gravity ° Bé.	52° F.	70° F.	89° F.	126° F.	155° F.	176° F.
c — c	Crude oil..	36.1	......	......	......	0.5192	......	......
o — o	Distillates:							
	I	65.1	......	0.4982	0.5094	......	......	......
	II	53.6	0.4751	0.4772	......	0.5328	......	......
	III	47.6	0.4706	0.4704	......	0.5210	0.5503	......
	IV	42.5	0.4655	0.4658	......	0.5159	......	......
G — G	Gas oil ...	27.6	......	......	......	0.5038	......	0.5338

[28] Redwood, "Treatise on Petroleum," 1913, 219-221.
[29] Bushong, F. W., & Knight, L. L., *J. Ind. Eng. Chem.*, 12 (1920), 1197-1200.

TABLE CVII—*Continued*

SPECIFIC HEATS OF PETROLEUMS AND PETROLEUM PRODUCTS [29a]

GULF COAST (TEXAS) PETROLEUM AND ITS PRODUCTS

		Gravity ° Bé.	52° F.	70° F.	86° F.	91° F.
c — c o — o	Crude oil	20.8	......	0.4406	......	......
	Distillates:					
	Solar	27.8	0.4150	0.4253	......	......
	L. L. D.	22.8	0.4135	0.4187	......	......
	H. L. D.	18.8	......	0.3905	0.4358	0.4385

		102° F.	126° F.	155° F.	176° F.
c — c o — o	Crude oil	0.4624	0.4823	......	......
	Distillates:				
	Solar	0.4532	0.4729	......	......
	L. L. D.	0.4465	0.4727	......	0.5207
	H. L. D.	0.4443	0.4724	0.4956	......

HYDROCARBONS

		25° C.	71.8° C.	88.3° C.
O_M	Octane	0.5052	......	......
O_L	Octane	......	0.5782	......
D_M	Isodecane	0.4951	......	......
D_L	Isodecane	......	......	0.5899

MEXICAN PETROLEUM AND ITS PRODUCTS

		Gravity ° Bé.	70° F.	102° F.	126° F.
c — c o — o	Crude oil	21.0	......	0.4667	0.4813
	Distillates:				
	I	60.6	0.5021	0.5197	0.5509
	II	50.1	0.4836	0.5055	0.5384
	III	42.4	0.4736	0.4983	0.5193
	IV	38.0	0.4715	0.4933	0.5103
G	Gas oil	11.9	......	......	0.4573

ROUMANIAN PETROLEUM PRODUCTS

Distillates:	16° C.
I	0.4840
II	0.4679
III	0.4652
IV	0.4619
Lubricating oil, 1	0.4579
Lubricating oil, 2	0.4567

[29a] Bushong, F. W., & Knight, L. L., *J. Ind. Eng. Chem.*, 12 (1920), 1197-1200.

TABLE CVII—*Continued*

SPECIFIC HEATS OF PETROLEUMS AND PETROLEUM PRODUCTS [29b]

RUSSIAN PETROLEUM PRODUCTS

Distillates:	17.5° C.	22.5° C.	27.5° C.	32.5° C.	37.5° C.
I	0.459	0.469	0.475	0.490	0.505
II	0.469	0.474	0.481	0.489	0.501
III	0.457	0.459	0.469	0.480	0.488
IV	0.449	0.459	0.460	0.463	0.465
Lubricating oil, 1	0.452	0.463	0.471	0.475	0.479
Lubricating oil, 2	0.550	0.550	0.559	0.566	0.571

TABLE CVIII

SPECIFIC HEATS OF HEAVY PETROLEUM FRACTIONS AT HIGH TEMPERATURES [30]

The specific heat of most fractions approximated 0.48 at 100° C., but rose to about 0.60 at 400° C. Between 100° C. and 400° C. the specific heat can be expressed with sufficient accuracy as a linear function of the temperature, i.e.,

$$\text{Sp. Ht.} = 0.4825 + 0.000385\ (t^\circ\ \text{C.} - 100^\circ\ \text{C.})$$

The specific heat of petroleum fractions of different specific gravity differed but slightly at the same temperatures.

TABLE CIX

LATENT HEAT OF VAPORIZATION OF A FEW HYDROCARBONS [31]

	Boiling point Degrees	Heat of Vaporization in Calories
Hexane, C_6H_{14}	68	79.4
Heptane, C_7H_{16}	98	74.
Octane, C_8H_{18}	125	71.1

Determinations were also made on the methylene hydrocarbons that could be volatilized in this form of apparatus:

	Boiling point Degrees	Heat in Calories
Hexamethylene, C_6H_{12}	68–70	87.3
Dimethylpentamethylene, C_7H_{14}	90–92	81.
Methylhexamethylene, C_7H_{14}	98	75.7
Dimethylhexamethylene, C_8H_{16}	118–119	71.7

TABLE CX

LATENT HEAT OF VAPORIZATION OF DISTILLATES [32]

	Latent Heat of Vaporization B.t.u. per pound
Gasoline 89° Bé.	100.2
Gasoline 65° Bé.	100.6
Naphtha 56° Bé.	103.5
Kerosene 43° Bé.	105.4

[29b] Bushong, F. W., & Knight, L. L., *J. Ind. Eng. Chem.*, 12 (1920), 1197-1200.
[30] *J. Soc. Chem. Ind.*, 33 (1914), 128.
[31] Mabery & Goldstein, *Proc. Am. Acad. Arts Sci.*, 37 (1902), 549.
[32] Redwood, "Treatise on Petroleum," 1913, 219-221.

TABLE CXI

KINEMATIC VISCOSITIES AT VARIOUS TEMPERATURES OF A SERIES OF PRODUCTS FROM CRUDE PETROLEUM [83]

Designation of Product	Description of Product			Kinematic Viscosities Determined at Indicated Temperatures									Kinematic Viscosities Calculated or Interpolated for Indicated Temperatures		
	Pressure under which Distilled	Temperature Limits of Cut		0° C. 32° F.	10° C. 50° F.	20° C. 68° F.	30° C. 86° F.	40° C. 104° F.	50° C. 122° F.	60° C. 140° F.	80° C. 176° F.	100° C. 212° F.	37.8° C 100° F.	54.4° C. 130° F.	98.9° C 210° F.
		° C.	° F.												
				A—Pennsylvania Crude											
P-A-125	Atmospheric	100–125	212–257	0.00880	0.00780	0.00703	0.00643	0.00593	0.00542	0.00508	0.00456	......	......	......	......
P-A-150	Atmospheric	125–150	257–302	0.0111	0.00957	0.00869	0.00780	0.00708	0.00649	0.00603	0.00524	0.00467	......	......	......
P-A-175	Atmospheric	150–175	302–347	0.0141	0.0121	0.0106	0.00946	0.00849	0.00769	0.00702	0.00618	0.00548	......	......	......
P-A-200	Atmospheric	175–200	347–392	0.0199	0.0166	0.0142	0.0123	0.0110	0.00964	0.00871	0.00737	0.00642	......	......	......
P-A-225	Atmospheric	200–225	392–437	0.0298	0.0236	0.0196	0.0167	0.0145	0.0127	0.0112	0.00926	0.00781	......	......	......
P-A-250	Atmospheric	225–250	437–482	0.0454	0.0345	0.0277	0.0227	0.0191	0.0164	0.0143	0.0115	0.00958	......	......	......
P-A-275	Atmospheric	250–275	482–527	0.0729	0.0529	0.0407	0.0322	0.0265	0.0221	0.0188	0.0147	0.0120	......	......	......
P-V-200	40-mm. vac.	175–200	347–392	0.1296	0.0884	0.0642	0.0489	0.0384	0.0315	0.0259	0.0195	0.0152	0.0400	0.0289	0.0153
P-V-225	40-mm. vac.	200–225	392–437	......	0.1372	0.0962	0.0704	0.0544	0.0432	0.0356	0.0247	0.0186	0.0574	0.0394	0.0188
P-V-250	40-mm. vac.	225–250	437–482	......	......	0.1533	0.1079	0.0798	0.0609	0.0484	0.0327	0.0238	0.0841	0.0546	0.0242
P-V-275	40-mm. vac.	250–275	482–527	......	......	......	0.1746	0.1225	0.0899	0.0694	0.0448	0.0312	0.1314	0.0797	0.0318
P-V-300	40-mm. vac.	275–300	527–572	......	......	......	......	0.2044	0.1444	0.1064	0.0654	0.0441	0.2245	0.1248	0.0450
P-R	Residuum				......	......	......	1.498	0.8064	0.5248	0.2581	0.1468	1.596	0.6780	0.1512
P-Mixt.	Mixture residuum and fraction P-V-225				......	......	......	0.1669	0.1208	0.0918	0.0570	0.0396	......	......	......
				B—California Crude											
C-A-125	Atmospheric	100–125	212–257	0.0103	0.00902	0.00807	0.00735	0.00665	0.00610	0.00565	0.00488	......	......	......	......
C-A-150	Atmospheric	125–150	257–302	0.0124	0.0108	0.00957	0.00860	0.00775	0.00711	0.00661	0.00570	0.00505	......	......	......
C-A-175	Atmospheric	150–175	302–347	0.0162	0.0138	0.0120	0.0106	0.00942	0.00847	0.00773	0.00651	0.00568	......	......	......
C-A-200	Atmospheric	175–200	347–392	0.0223	0.0185	0.0158	0.0135	0.0119	0.0105	0.00943	0.00781	0.00673	......	......	......
C-A-225	Atmospheric	200–225	392–437	0.0332	0.0263	0.0215	0.0180	0.0154	0.0134	0.0120	0.00961	0.00817	......	......	......
C-A-250	Atmospheric	225–250	437–482	0.0523	0.0396	0.0312	0.0252	0.0210	0.0179	0.0154	0.0121	0.00987	......	......	......
C-A-275	Atmospheric	250–275	482–527	0.0935	0.0656	0.0486	0.0375	0.0302	0.0249	0.0209	0.0158	0.0124	......	......	......
C-V-200	40-mm. vac.	175–200	347–392	0.2142	0.1328	0.0902	0.0645	0.0485	0.0383	0.0308	0.0217	0.0165	0.0510	0.0348	0.0166
C-V-225	40-mm. vac.	200–225	392–437	......	0.2825	0.1717	0.1136	0.0803	0.0596	0.0459	0.0303	0.0219	0.0818	0.0529	0.0222
C-V-250	40-mm. vac.	225–250	437–482	......	0.8393	0.4360	0.2548	0.1628	0.1122	0.0807	0.0482	0.0322	0.1766	0.0962	0.0328
C-V-275	40-mm. vac.	250–275	482–527	......	......	......	0.0926	0.3877	0.2372	0.1572	0.0825	0.0502	0.4380	0.1961	0.0514
C-V-300	40-mm. vac.	275–300	527–572	......	......	......	......	0.8282	0.4612	0.2836	0.1305	0.0736	0.9363	0.3686	0.0757
P-C-Mixt.	Mixture of Pennsylvania residue and C-V-250			......	......	......	......	0.3228	0.2108	0.1465	0.0811	0.0517	......	......	......

C—Wyoming Crude

W-A-125	Atmospheric	100–125	212–257	0.00927	0.00829	0.00741	0.00675	0.00609	0.00567	0.00533	......	......	......	......	......
W-A-150	Atmospheric	125–150	257–302	0.01141	0.00999	0.00890	0.00803	0.00730	0.00669	0.00622	0.00547	0.00489	......	......	......
W-A-175	Atmospheric	150–175	302–347	0.0151	0.0129	0.0113	0.0100	0.00895	0.00808	0.00752	0.00628	0.00547	......	......	......
W-A-200	Atmospheric	175–200	347–392	0.0207	0.0173	0.0148	0.0128	0.0114	0.0101	0.00907	0.00760	0.00646	......	......	......
W-A-225	Atmospheric	200–225	392–437	0.0299	0.0241	0.0200	0.0169	0.0146	0.0127	0.0114	0.00919	0.00773	......	......	......
W-A-250	Atmospheric	225–250	437–482	0.0452	0.0348	0.0281	0.0231	0.0193	0.0165	0.0143	0.0114	0.00935	......	......	......
W-A-275	Atmospheric	250–275	482–527	0.0737	0.0542	0.0414	0.0327	0.0268	0.0224	0.0191	0.0146	0.0116	......	......	......
W-V-200	40-mm. vac.	175–200	347–392	0.1432	0.0976	0.0698	0.0526	0.0412	0.0330	0.0274	0.0199	0.0155	0.0433	0.0303	0.0157
W-V-225	40-mm. vac.	200–225	392–437	......	0.1491	0.1026	0.0743	0.0563	0.0442	0.0356	0.0251	0.0188	0.0596	0.0401	0.0101
W-V-250	40-mm. vac.	225–250	437–482	......	......	0.1792	0.1227	0.0892	0.0672	0.0528	0.0356	0.0257	0.0955	0.0600	0.0260
W-V-275	40-mm. vac.	250–275	482–527	......	......	......	0.2070	0.1418	0.1033	0.0774	0.0483	0.0334	0.154	0.0905	0.0340
W-V-300	40-mm. vac.	275–300	527–572	......	......	......	......	0.2501	0.1701	0.1230	0.0723	0.0470	0.274	0.146	0.0480

[88] Dean, E. W., & Lane, F. W., *J. Ind. Eng. Chem.*, 13 (1921), 779-86.

TABLE CXII

SAYBOLT UNIVERSAL VISCOSITIES AT VARIOUS TEMPERATURES OF A SERIES OF PRODUCTS FROM CRUDE PETROLEUM [34]

(Fractions distilled at 40-mm. vacuum)

Designation of Fraction	Temperature Limits of Fraction		Saybolt Viscosities											
	° C.	° F.	0° C. 32° F.	10° C. 50° F.	20° C. 68° F.	30° C. 86° F.	40° C. 104° F.	50° C. 122° F.	60° C. 140° F.	80° C. 176° F.	100° C 212° F.	37.8° C. 100° F.	54.4° C. 130° F.	98.9° C. 210° F.
A—Pennsylvania Crude														
P-V-200	175–200	347–392	70.5	55.0	46.7	41.8	38.6	36.6	35.1	33.4	32.3	39.1	35.9	32.3
P-V-225	200–225	392–437	....	73.5	57.9	48.8	43.5	40.1	37.8	34.8	33.1	44.5	38.9	33.2
P-V-250	225–250	437–482	....	....	79.9	62.2	52.0	45.6	41.7	37.0	34.5	53.5	43.6	34.6
P-V-275	250–275	482–527	....	....	....	88.6	67.8	55.6	48.4	40.5	36.6	71.2	52.0	36.7
P-V-300	275–300	527–572	....	....	....	....	101.0	76.4	61.6	47.1	40.3	109.5	68.7	40.6
P-R	Residuum		....	....	....	....	682.2	368.8	241.6	123.9	77.3	726.8	310.8	79.1
P-Mixt	Mixture P-R and P-V-225		....	....	....	....	85.5	67.1	56.2	44.3	39.0	....	....	....
B—California Crude														
C-V-200	175–200	347–392	105.1	71.8	55.7	46.8	41.7	38.6	36.4	33.9	32.6	42.5	37.6	32.6
C-V-225	200–225	392–437	....	134.5	87.4	64.3	52.2	45.2	40.9	36.3	34.0	53.8	43.1	34.1
C-V-250	225–250	437–482	....	383.5	202.2	122.5	83.8	63.8	52.3	41.6	36.8	89.4	57.9	37.0
C-V-275	250–275	482–527	....	....	....	317.5	180.7	114.9	81.5	53.0	42.2	203.1	97.5	42.6
C-V-300	275–300	527–572	....	....	....	....	378.7	213.5	135.0	70.8	49.9	427.5	172.3	50.6
P-C-Mixt	Mixture P-R and C-V-250		....	....	....	....	152.1	103.7	77.2	52.5	42.8	....	....	....
C—Wyoming Crude														
W-V-200	175–200	347–392	75.9	58.4	48.6	43.0	30.5	37.1	35.5	33.5	32.3	40.1	36.3	32.4
W-V-225	200–225	392–437	....	78.3	60.2	50.1	44.2	40.3	37.8	34.8	33.3	45.2	39.1	33.3
W-V-250	225–250	437–482	....	....	90.5	67.8	55.3	47.6	43.0	37.8	35.0	57.6	45.3	35.1
W-V-275	250–275	482–527	....	....	....	102.1	75.3	60.5	41.6	51.2	37.2	80.2	55.8	37.4
W-V-300	275–300	527–572	....	....	....	....	120.5	86.7	68.0	49.4	41.2	130.8	77.0	41.5

[34] Dean, E. W., & Lane, F. W., *J. Ind. Eng. Chem.*, 13 (1921), 779-86.

The original article should be consulted for details and much useful information that cannot be included here for lack of space. A showing of the data in the form of curves is given, and a method of calculating viscosities at various temperatures is developed. This note also applies to Table CXII.

TABLE CXIII

FLUIDITIES OF GASOLINES[35]

Gasoline No.	Specific Gravity 15.6° C. / 15.6° C.	Temperature: 5° C.	15° C.	25° C.	35° C.	45° C.	55° C.
		Fluidities as Reciprocals of Viscosities in Poises					
1	0.757	145	166	193	212	235	262
2	.748	130	151	170	194	214	243
3	.743	129	156	185	203	227	....
4	.726	202	233	264	293	324	360*
5	.722	189	219	244	278	308	342*
6	.717	176	208	239	277	295	....
7	.716	197	217	256	280	321	341*
8	.708	203	230	257	298	332	360*
9	.702	233	261	296	321	358*	400*
10	.701	230	262	287	333	373*	398*
11	.699	233	269	306	335	372*	423*
12	.694	251	286	316	354*	387*	427*
13	.680	288	323	365*	413*	441*	475*
Kerosene	.813	39	47	61	71	84	....

* Fluidities calculated from discharge times of less than 155 seconds.

TABLE CXIV

FLUIDITIES OF KEROSENES[36]

Authority	Liquid	Specific Gravity 15.6° C. / 15.6° C.	Fluidity* at 20° C.
Ubbelohde	Kerosene C	0.799	61.6
Do	Kerosene E	.799	52.8
Do	Kerosene A	.808	64.9
Do	Kerosene B	.808	70.2
Do	Kerosene O	.809	52.8
Do	Kerosene (German)	.816	68.5
Do	Kerosene F	.817	44.2
Do	Nobel kerosene	.823	55.3
Post	American water-white kerosene	.790	49.3
Do	American Standard white "	.800	42.1
Do	Russian "meteor" kerosene	.800	59.7
Do	Galician kerosene	.809	44.3
Do	German kerosene	.810	43.6
Do	Russian "nobel" kerosene	.824	47.3

* Fluidities are given as the reciprocals of the viscosities in poises.

[35] U. S. Bur. Standards, Tech. Paper 125, 16.

[36] U. S. Bur. Standards, Tech. Paper 125, 15. Post's *Chem. Tech. Analyses*, I, 317-8.

TABLE CXV

COMPRESSIBILITY OF KEROSENE AT 20° C.[37]

Pressure Megabars	Fractional Change of Volume between 2,000 Megabars and P. Megabars
12,000	0.150
11,000	0.142
10,000	0.133
9,000	0.123
8,000	0.111
7,000	0.098
6,000	0.084
5,000	0.068
4,000	0.050
3,000	0.027
2,000	0.000

TABLE CXVI

VOLUME OF WATER AS A FUNCTION OF TEMPERATURE AND PRESSURE[38]

Pressure kg. per sq. cm.	0° C.	Volume 20° C.	40° C.
0	1.0000	1.0016	1.0076
500	.9771	.9808	.9873
1,000	.9578	.9630	.9700
2,000	.9260	.9327	.9403
3,000	.9015	.9087	.9164
4,000	.8807	.8880	.8956
5,000	.8632	.8702	.8778
6,000	.8480	.8545	.8623
7,000	.....	.8404	.8485
8,000	.....	.8275	.8360
9,000	.....	.8160	.8249
10,000	.....	.....	.8149
11,000	.....	.....	.8056
12,000	.....	.....	.7966
12,500	.....	.....	.7922

[37] Williamson, E. D., Paper No. 446, Geophys. Lab. Carn. Inst. Wash., 505.
[38] Williamson, E. D., Paper No. 446, Geophys. Lab. Carn. Inst. Wash., 504.

TABLE CXVII

SURFACE TENSION OF PETROLEUMS FROM DIFFERENT FIELDS IN THE U. S.[39]

Source	Base of Oil	Color	Sp. Gr.	Surface Tension *	
				Bé.°	Dynes/Cm. @ 85° F.
Cabin Creek, W. Va.	Paraffin	Yellow	0.7865	48.0	28.8
Winnette, Mont.	....	Very Dark Green	0.7937	46.4	29.0
Cushing, Okla.	Semi-Paraffin	Very Dark Green	0.8279	39.1	29.7
Osage, Okla. ..	Semi-Paraffin	Dark Green	0.8403	36.6	30.7
Bixby, Okla. ..	Semi-Paraffin	Very Dark Green	0.8444	35.8	30.8
Homer, La. ...	Semi-Paraffin	Very Dark Green	0.8464	35.4	31.2

* Used duNouy Apparatus.

TABLE CXVIII

SURFACE TENSIONS, VISCOSITIES, AND BOILING RANGE OF LIGHTER DISTILLATES FROM PETROLEUMS[40]

Bé. Gravity	Boiling Point, ° F.		Viscosity[a]		Surface Tension, Dynes per Cm. at ° F.				
	Initial	Max.	60° F.	90° F.	60	70	80	85	90
62.4	108	392	...	...	...	...	...	24.4	...
60.6	106	404	125	...	26.9	26.4	25.6	...	...
59.3	111	426	...	...	...	...	...	24.9	...
59.1	96	449	...	...	...	...	...	24.8	...
58.9	120	426	...	...	...	...	...	25.3	...
58.6	114	434	...	...	...	...	...	25.3	...
58.4	100	412	...	...	...	...	...	25.3	...
58.4	110	434	...	...	...	...	...	25.6	...
57.4	131	436	...	...	...	...	...	25.7	...
57.3	100	448	...	...	27.6	27.3	26.9	...	...
57.1	116	429	...	...	...	...	...	24.8	...
57.1	110	450	...	...	...	...	...	25.7	...
56.8	118	440	143	...	27.6	27.1	26.6	...	...
56.9	120	436	...	...	...	...	...	25.8	...
56.3	106	450	...	...	...	...	...	25.8	...
55.7	140	439	154	...	27.8	27.5	27.0	...	...
55.2	126	454	...	...	...	...	...	26.3	...
54.3	146	442	...	...	...	...	...	27.4	...
48.3[b]	132	558	...	...	...	...	...	28.2	...
46.7	224	466	...	...	...	...	...	29.2	...
45.9	146	608	249	...	30.0	29.5	29.0	...	...
43.9[b]	146	558	...	...	...	...	...	29.1	...
42.2	326	490	320	247	31.9	31.9	30.9	...	30.5
41.5	344	575	419	312	32.7	31.9	31.2	...	30.9
39.5	380	612	545	396	33.1	32.4	31.9	...	31.4

[a] Viscosity determined with Saybolt Thermo Viscometer.

[b] Cracked product.

[39] Francis, C. K., & Bennett, H. T., *J. Ind. Eng. Chem.*, 14 (1922), 627.

[40] Francis, C. K., & Bennett, H. T., *J. Ind. Eng. Chem.*, 14 (1922), 627.

TABLE CXIX

Surface Tension of Petroleum Products[41]

Product	Gravity	Surface Tension at 85° F. Dynes/Cm.
Crude	35.4-48.0	28.8-31.2
Gasoline	56.3-62.4	24.4-25.8
Naphtha	46.7-55.2	26.3-29.2
Kerosene	40.2-42.4	30.7-31.2
Gas Oil	35.9	33.1
Lubricating Oil	19.7-27.1	36.0-37.5
Wax Distillate	27.5-33.2	33.6-36.2

TABLE CXX

Surface Tension, Viscosity, and Specific Gravity of Lubricants[42]

Product	Bé. Gravity	Cold Test	Saybolt Universal Viscosity at 100° F.	Color N. P. A.	Surface Tension Dynes/Cm. at 85° F.
Oklahoma Lubricating Oil	27.1	23	155	2—	36.0
Oklahoma Lubricating Oil	27.2	25	160	3—	36.2
Oklahoma Lubricating Oil	26.2	26	185	4—	36.0
Oklahoma Lubricating Oil	25.8	25	240	6—	36.4
Oklahoma Lubricating Oil	25.5	19	260	Q+	37.5
Oklahoma Cylinder Stock	23.8	24	1160	Green	37.3
California Lubricating Oil	19.7	—0	428	4.5—	37.3
Castor Oil	15.9	10	100 at 210° F.	2	40.4

TABLE CXXI

The Flash Point of Gasoline[43]

"Pratt's" Motor-Spirit (essentially a "closed" test)	=—30° C.
"Standard" Spirit (essentially a "closed" test)	=—11° C.
"Shell" Spirit (essentially a "closed" test)	=—16° C.

[41] Francis, C. K., & Bennett, H. T., *J. Ind. Eng. Chem.*, 14 (1922), 628.
[42] Francis, C. K., & Bennett, H. T., *J. Ind. Eng. Chem.*, 14 (1922), 627.
[43] Coste, J. H., *Analyst*, 42 (1917), 168-70.

The Freezing Point of Gasoline.

Gasoline[44] of 0.698 sp. gr. at 22.8° C. was found to be slightly pasty at — 122° C., and to resemble a viscous oil at — 125° C. As the temperature was lowered the gasoline rapidly became harder.

Another gasoline of 0.713 sp. gr. at 22.8° C. became slightly pasty at — 120° C. and at — 147° C. it was a horn-like solid. There was no sign of crystallization.

Pratts' motor spirit was found by Coste[45] to solidify at — 128° C. A slight opalescence was observed before the distillate became solid.

Molecular Weights of Benzines.[46]

The measurements were made by the freezing-point lowering method. The investigated benzine fractions were obtained from Boryslaw crude benzine, and were fractionated by means of the Glinsky dephlegmator until they distilled within the limit of 1° C. C_6H_6 was employed as solvent. The following results were obtained:

Sp. Gr.	B. P.	Concentration	Mol. Wt.
0.6520	50°	0.264	80.0
0.7500	110°	0.354	103.0
0.7690	130°	0.385	116.6
0.7796	160°	.....	130.5
0.8229	250°	0.569	186.5

Electrical Conductivity of Petroleum Products.

Benzine[47] .... 2×10^{-12} reciprocal ohms.
Benzines and Petroleum Ethers[48]....... 1×10^{-14} to 1×10^{-15}

Solubility of Water in Gasoline, Kerosene and Paraffin Oil.[49]

The solubility of water in gasoline, kerosene, and paraffin oil is shown in Figure 166.

Variation of Boiling Point of Distillates with Pressure Altitude.[50]

Boiling points of benzine and kerosene were determined at Minatitlan, Mexico, at sea level (pressure 765 mm.), Jalapa, Mexico, 1400 meters above sea-level (pressure 650 mm.), and at Mexico City, 2250 meters above sea-level (pressure 590 mm.).

[44] Cabot, G. L., *J. Soc. Chem. Ind.*, 26 (1908), 813.
[45] Coste, J. H., *Analyst.*, 42 (1917), 168-70.
[46] Ogrodzinski, W., & St. von Pilat, *Pet.*, 8, 1181-2.
[47] Richter, M. M., *Chem. Ind.*, 35 (1912), 833-5.
[48] Holde, O., *Seifen Fabr.*, 35 (1915), 182-4, 207-9.
[49] Clifford, C. W., *J. Ind. Eng. Chem.*, 13 (1921), 631-2.
[50] Lohmann, D., *Chem. Ztg.*, 38 (1914), 897-8.

An average difference of 0.038° C. for benzine and 0.032° C. for kerosene was found for each millimeter difference in pressure. This is lower than the commonly used figure of 0.045° C. per millimeter.

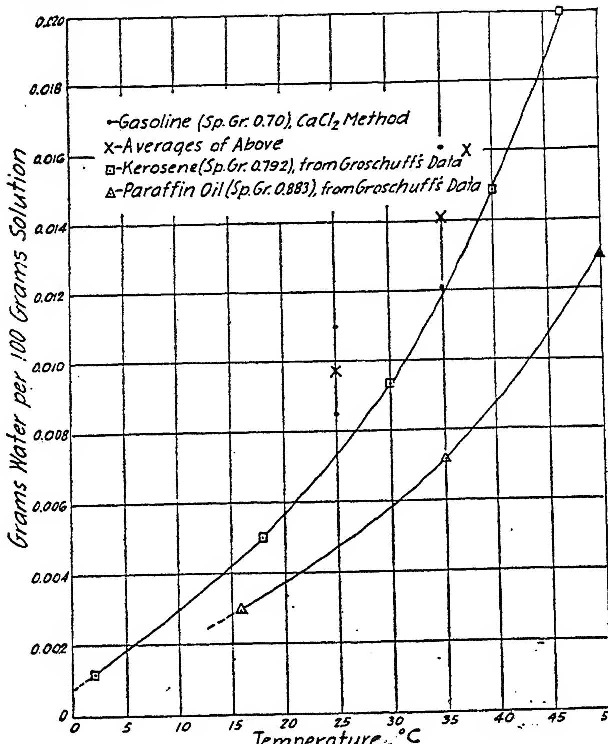

FIG. 166.—Solubility of Water in Petroleum Products.

R. Kissling [51] found that a change of 30 mm. in pressure caused a change of 1.2° C. in the boiling point of petroleum ether, 1.4° C. in the boiling point of light benzine, and 1.6° C. in the boiling point of heavy benzine.

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[51] *Chem. Ztg.*, 32 (1908), 695.

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AUTHOR INDEX

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